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The Optimized Effective Potential Method and LDA + U

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The fundamental quantity of density functional theory is the exchange-correlation energy functional. The exact form of this functional is unknown and it has to be approximated in practice. The exchange-correlation potentials corresponding to approximate functionals which depend explicitly on the Kohn-Sham orbitals have to be computed with the optimized effective potential (OEP) method. Here, the OEP method is reviewed and commonly used orbital functionals are introduced. One particular approach, the so-called LDA+U method which is often applied to describe strongly correlated systems is discussed from the OEP perspective. Finally, a few selected numerical results for atoms, molecules, and solids are presented.

1 Introduction

Density functional theory (DFT) has become the most widely used tool to study the electronic structure of atoms, molecules and solids. As it is used today, it essentially is an ingenious reformulation of the many-body problem. Instead of trying to solve the Schrödinger equation of interacting electrons directly, the problem is cast in a way such as to make it tractable in an approximate, but in many cases surprisingly accurate way. The success of DFT is largely due to the availability of increasingly accurate approximations to the central quantity of DFT, the so-called exchange-correlation energy functional. While the simple local density approximation (LDA) proved to be surprisingly accurate especially in solid state physics, only the advent of the so-called generalized gradient approximations (GGA's) with their increased accuracy led to an explosion of applications of DFT in quantum chemistry.

The development of new, improved functionals is an ongoing effort. In this contribution we are dealing with a particular class of approximations which are explicit functionals of the Kohn-Sham orbitals rather than explicit functionals of the density (such as LDA or GGA). Treatment of orbital functionals in the DFT framework requires the use of the so-called optimized effective potential (OEP) method to compute the corresponding effective single-particle potentials. Here, we will review this method, and derive its central equation. Several approximate and exact schemes to solve this equation will be discussed as well as some properties of the resulting potentials. An extension of the OEP method for the description of non-collinear magnetism will briefly be described.

We discuss possible ways to construct orbital functionals and present some of them which have been used in the literature. Furthermore, we discuss a connection between orbital functionals and the so-called LDA+U method. This method tries to combine insights gained from studies of model Hamiltonians into the DFT framework in order to describe strongly correlated systems. Finally, we discuss some numerical results obtained with orbital functionals for atoms, molecules, and solids.

2 Kohn-Sham Density Functional Theory

We are interested in systems of N interacting electrons moving in some external electrostatic potential $v(\mathbf{r})$. The Hamiltonian to describe such systems is given by (atomic units are used throughout)

$$\hat{H} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2} + \sum_{i=1}^{N} v(\mathbf{r}_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} := \hat{T} + \hat{V} + \hat{V}_{ee} \tag{1}$$

with the kinetic energy operator $\hat{T}$, the potential energy $\hat{V}$ and the operator $\hat{V}_{ee}$ of the electron-electron interaction.

The first key insight is given by the Hohenberg-Kohn theorem[1] which states that the ground-state energy of a system of interacting electrons can be written as a functional of the electron density $n(\mathbf{r})$ alone and takes its minimum at the true ground state density. This functional can be written as

$$E_v[n] = F[n] + \int \mathrm{d}^3 r \; v(\mathbf{r}) n(\mathbf{r}) \tag{2}$$

where $F[n]$ is a *universal* functional of the density, i.e., it is independent of the external potential $v(\mathbf{r})$ and therefore it is the same functional of the density for all Coulombic systems such as atoms, molecules and solids. Using the "constrained search" formulation of Levy[2,3], this functional may formally be defined as

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle = \langle \Psi_n^{\min} | \hat{T} + \hat{V}_{ee} | \Psi_n^{\min} \rangle \tag{3}$$

where the search runs over all possible, antisymmetric N-electron wave functions which yield the density $n(\mathbf{r})$ and $\Psi_n^{\min}$ is the minimizing wave function.

Eq. (3) is a purely formal definition and cannot be used in practice to find the minimizing density of Eq. (2). To make the Hohenberg-Kohn density variational principle practical, Kohn and Sham[4] suggested to construct a system of non-interacting electrons in such a way that the ground state density of the auxiliary non-interacting system is equal to the ground state density of the interacting system. To this end, $F[n]$ is partitioned as

$$F[n] = T_s[n] + U[n] + E_{xc}[n] \tag{4}$$

where $T_s[n]$ is the kinetic energy functional of *non-interacting* electrons with density n and

$$U[n] = \frac{1}{2} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \; \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{5}$$

is the classical electrostatic or Hartree energy of the charge distribution $n(\mathbf{r})$. $E_{xc}[n]$ is the so-called exchange-correlation (xc) energy functional which will be the main quantity of interest later in this work. Using this decomposition the total energy functional (Eq. (2)) may be written as

$$E_v[n] = T_s[n] + \int \mathrm{d}^3 r \; v(\mathbf{r}) n(\mathbf{r}) + U[n] + E_{xc}[n] \tag{6}$$

The Hohenberg-Kohn theorem can also be applied to non-interacting electrons moving in some potential $v_s(\mathbf{r})$. The corresponding ground-state energy functional then reads

$$E_{v_s}^{non-int}[n] = T_s[n] + \int \mathrm{d}^3 r \; v_s(\mathbf{r}) n(\mathbf{r}) \; . \tag{7}$$

Due to the Hohenberg-Kohn variational principle one can determine the ground state density of this non-interacting system by minimizing the functional (Eq. (7)), i.e.,

$$\frac{\delta E_{v_s}^{non-int}[n]}{\delta n(\mathbf{r})} = 0 \; . \tag{8}$$

Alternatively, however, we can also determine the ground state density of a system of N non-interacting electrons by solving the single-particle Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) \right) \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r}) \tag{9}$$

and compute the density from the $N = N_\uparrow + N_\downarrow$ orbitals with lowest energy eigenvalues $\varepsilon_{i\sigma}$ by

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \; . \tag{10}$$

Here, N_σ is the total number of electrons with spin σ. Applying the variational principle to the energy functional (Eq. (6)) one realizes that the resulting variational equation has the same structure as the one for non-interacting electrons if one defines an effective potential

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \tag{11}$$

with the Hartree potential

$$v_H(\mathbf{r}) = \frac{\delta U[n]}{\delta n(\mathbf{r})} = \int \mathrm{d}^3 r' \; \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{12}$$

and the exchange-correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \; . \tag{13}$$

As a consequence, the ground state density of the *interacting* system may also be calculated by solving the single-particle equation (9) with the effective potential given by Eq. (11). Since v_H and v_{xc} depend on the density (10), the whole procedure has to be solved self-consistently. This constitutes the Kohn-Sham scheme of density functional theory[4].

It is worth noting that this scheme in principle yields the exact ground state density and, via Eq. (6), also the exact ground state energy, provided that the exact exchange-correlation energy functional $E_{xc}[n]$ is used. This exchange-correlation functional is something like the holy grail of density functional theory: although its formal definition has already been given in the original work of Hohenberg and Kohn[1] and further been clarified in the constrained-search formulation of Levy[2,3], these definitions cannot be used in practice and one needs to resort to approximations.

Fortunately, it is possible to construct simple approximations which perform, sometimes surprisingly, well. The first and probably most widely known approximation is the

so-called Local Density Approximation (LDA), which is based on the model of the uniform electron gas. Formally, the LDA is defined as

$$E_{xc}^{LDA}[n] = \int \mathrm{d}^3 r \; n(\mathbf{r}) \epsilon_{xc}^{unif}(n(\mathbf{r})) \tag{14}$$

where $\epsilon_{xc}^{unif}(n)$ is the exchange-correlation energy per electron of the uniform electron gas with (constant) density n. This function is known from Quantum Monte Carlo calculations[5] and several simple parametrizations have been suggested[6–8]. Despite its simplicity, LDA has proven to be surprisingly accurate and hard to improve.

A major breakthrough in the development of more accurate exchange-correlation functionals came with the advent of so-called "generalized gradient approximations" (GGA's) which have the general form

$$E_{xc}^{GGA}[n] = \int \mathrm{d}^3 r \; f(n, \nabla n) \; . \tag{15}$$

While the input $\epsilon_{xc}^{unif}(n)$ in LDA is unique, the function $f(n, \nabla n)$ in Eq. (15) is not and many forms have been suggested[9–17]. Although LDA had already widely been used in solid state physics, only with the increased accuracy of the GGA's the Kohn-Sham scheme became a standard tool for electronic structure calculations in theoretical chemistry as well.

3 Orbital Functionals and the Optimized Effective Potential Method

The explicit dependence on the density is known both for LDA and GGA functionals. More recently, it has been recognized that functionals depending explicitly on the Kohn-Sham orbitals may also be viewed as density functionals since the orbitals are, through Eq. (9), functionals of the density-dependent effective potential $v_s(\mathbf{r})$. Since the explicit dependence of the orbitals on the density remains unknown, these orbital functionals are sometimes called *implicit* density functionals.

The idea of implicit density functionals might appear surprising at first sight. However, this idea is already used in the original Kohn-Sham formalism because the kinetic energy $T_s[n]$ of the non-interacting system may be expressed without approximation in terms of the Kohn-Sham orbitals, i.e.,

$$T_s[n] = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \int \mathrm{d}^3 r \; \varphi_{i\sigma}^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi_{i\sigma}(\mathbf{r}) \; . \tag{16}$$

Turning to the exchange-correlation energy one also realizes that orbital-dependent expressions provide a natural framework for approximations to E_{xc}: if one performs a power series expansion of the functional $E_{xc}[n]$ in terms of the interaction strength e^2 (where e is the elementary charge) one obtains as leading term in this series the exact exchange energy. This term is a known explicit functional of the orbitals and reads as

$$E_x^{EXX}[n] = E_x^{EXX}[\{\varphi_i\}] = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k=1}^{N_\sigma} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \frac{\varphi_{j\sigma}^*(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \tag{17}$$

which is nothing but the Fock exchange energy but evaluated with Kohn-Sham orbitals. The derivation of Eq. (17) as well as possible routes to go beyond exchange will be discussed in more detail in Section 4.

3.1 Optimized Effective Potential Equation: Two Derivations

Once we accept to use an expression for E_{xc} which explicitly depends on the Kohn-Sham orbitals, the main question is how to compute the corresponding exchange-correlation potential of Eq. (13).

The way to accomplish this task is indicated by the Hohenberg-Kohn theorem. Application of this theorem to the Kohn-Sham system shows that there is a one to one correspondence between $n(\mathbf{r})$ and $v_s(\mathbf{r})$. The latter, in turn, determines the Kohn-Sham orbitals from which the density can be obtained. Thus, we can formally write any of these quantities as functional of one of the other quantities and an explicit dependence on one of them introduces an implicit dependence on the others. We use this observation in order to rewrite Eq. (13) using the chain rule of functional differentiation as follows

$$v_{xc}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \left(\frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta n(\mathbf{r})} + c.c. \right) . \tag{18}$$

For simplicity, we assumed here that the exchange-correlation functional is given as a functional of the occupied Kohn-Sham orbitals only. The functional derivative of E_{xc} with respect to the orbitals can easily be calculated from its explicit functional form. In order to calculate the functional derivative of the orbitals with respect to the density, we now view the orbitals as functional of $v_s(\mathbf{r})$ and use, for a second time, the chain rule of functional differentiation to obtain

$$v_{xc}(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' \left(\frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r}'')} \frac{\delta v_s(\mathbf{r}'')}{\delta n(\mathbf{r})} + c.c. \right) . \tag{19}$$

The third functional derivative on the right hand side of this equation may now be identified as the inverse of the static density response function of the Kohn-Sham system defined by

$$\chi_s(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} . \tag{20}$$

Operating with χ_s on Eq. (19) from the right one obtains

$$\int \mathrm{d}^3 r' v_{xc}(\mathbf{r}') \chi_s(\mathbf{r}', \mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \int \mathrm{d}^3 r' \left(\frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right) . \tag{21}$$

Now all the terms in this equation can be expressed in terms of the Kohn-Sham orbitals and eigenvalues. The functional derivative of the orbitals with respect to the potential can be obtained exactly from first order perturbation theory and reads

$$\frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} = G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \tag{22}$$

where we have defined

$$G_{s,j\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{\substack{k \\ k \neq j}} \frac{\varphi_{k\sigma}(\mathbf{r}) \varphi^*_{k\sigma}(\mathbf{r}')}{\varepsilon_{j\sigma} - \varepsilon_{k\sigma}} . \tag{23}$$

For simplicity, we have assumed here that the single-particle levels are non-degenerate. The static linear density response function of the Kohn-Sham system may be written as

$$\chi_s(\mathbf{r},\mathbf{r}') = \sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\left(\varphi^*_{j\sigma}(\mathbf{r})G_{s,j\sigma}(\mathbf{r},\mathbf{r}')\varphi_{j\sigma}(\mathbf{r}') + c.c.\right) \ . \tag{24}$$

Substituting (22) and (24) into Eq. (21) yields

$$\sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\int \mathrm{d}^3r' \left(\varphi^*_{j\sigma}(\mathbf{r}')\big(v_{xc}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')\big)G_{s,j\sigma}(\mathbf{r}',\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) + c.c.\right) = 0 \tag{25}$$

where we have defined

$$u_{xc,j\sigma}(\mathbf{r}') := \frac{1}{\varphi^*_{j\sigma}(\mathbf{r}')}\frac{\delta E_{xc}}{\delta\varphi_{j\sigma}(\mathbf{r}')} \ . \tag{26}$$

Introducing the so-called orbital shifts[18–20]

$$\psi^*_{j\sigma}(\mathbf{r}) := \int \mathrm{d}^3r'\varphi^*_{j\sigma}(\mathbf{r}')\big(v_{xc}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')\big)G_{s,j\sigma}(\mathbf{r}',\mathbf{r}) \tag{27}$$

allows to rewrite Eq. (25) in a very compact way

$$\sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\left(\psi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) + c.c.\right) = 0 \tag{28}$$

which is the standard form of the so-called Optimized Effective Potential (OEP) equation.

The name of this equation suggests that the resulting potential is optimal, but in which sense is it so? In DFT, the value of the ground-state total energy corresponds to the minimum value of the total energy functional. This minimum is obtained only if the exact ground-state particle density is inserted. Now the idea of the Kohn-Sham method is that the density can be obtained from single-particle orbitals solving a single-particle Schrödinger equation. Hence, in order to produce those single-particle orbitals we need to use a proper single-particle potential which is nothing but the optimized effective potential. Formally, this potential follows from minimizing the total energy functional (Eq. (6)). Using again the chain rule one obtains

$$\frac{\delta E_v}{\delta v_s(\mathbf{r})} = \int \mathrm{d}^3r' \frac{\delta E_v}{\delta n(\mathbf{r}')}\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} = 0 \tag{29}$$

where the last equality follows from the Hohenberg-Kohn variational principle, Eq. (8).

Interpreting $E_v[n]$ now as a functional of the orbitals, Eq. (29) may be written as

$$0 = \frac{\delta E_v}{\delta v_s(\mathbf{r})} = \sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma}\int \mathrm{d}^3r' \left(\frac{\delta E_v}{\delta\varphi^*_{j\sigma}(\mathbf{r})}\frac{\delta\varphi^*_{j\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c.\right) \ . \tag{30}$$

The functional derivative of E_v with respect the Kohn-Sham orbitals is easily expressed as

$$\frac{\delta E_v}{\delta\varphi^*_{j\sigma}(\mathbf{r})} = \left(-\frac{\nabla^2}{2} + v(\mathbf{r}) + v_H(\mathbf{r})\right)\varphi_j(\mathbf{r}) + \frac{\delta E_{xc}}{\delta\varphi^*_{j\sigma}(\mathbf{r}')} \tag{31}$$

which, by using the Kohn-Sham equation, may be expressed as

$$\frac{\delta E_v}{\delta \varphi^*_{j\sigma}(\mathbf{r})} = \left(\varepsilon_{j\sigma} - v_{xc}(\mathbf{r})\right)\varphi_j(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \varphi^*_{j\sigma}(\mathbf{r}')} \; . \tag{32}$$

Inserting this expression into Eq. (30) and using the orthonormality of the Kohn-Sham orbitals, one finally arrives at the integral equation (25) for $v_{xc}(\mathbf{r})$. In other words, the optimized effective potential is that *local* potential which yields single-particle orbitals which minimize the total energy[21,22]. This potential is nothing but the Kohn-Sham potential[23,24].

3.2 Solution of the OEP Equation: KLI and CEDA Approximation

The OEP equation (25) is an integral equation to be solved for the exchange-correlation potential $v_{xc}(\mathbf{r})$. Historically, this solution first has been achieved for systems with very high symmetry[22]. In order to reduce the computational effort, simplifying yet accurate approximations to the full OEP equations have been suggested which will be discussed in this section.

We see that an important ingredient of the OEP equation is the Green function of Eq. (23) which involves a summation over occupied and unoccupied Kohn-Sham orbitals. Sharp and Horton[21] and later Krieger, Li, and Iafrate (KLI)[25,26] proposed to approximate the Green function (Eq. (23)) by replacing the energy denominators by a constant value, independent of the particle indices j and k. Using the completeness of the Kohn-Sham orbitals, this approximation leads to

$$\begin{aligned} G^{KLI}_{s,j\sigma}(\mathbf{r},\mathbf{r}') &= \frac{1}{\Delta}\Big(\sum_{k=1}^{\infty}\varphi^*_{k\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}') - \varphi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')\Big) \\ &= \frac{1}{\Delta}\Big(\delta(\mathbf{r}-\mathbf{r}') - \varphi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')\Big) \; . \end{aligned} \tag{33}$$

Substitution into Eq. (27) gives

$$\sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma} n_{j\sigma}(\mathbf{r})\left(v^{KLI}_{xc}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - \left(\overline{v}^{KLI}_{xc,j\sigma} - \overline{u}_{xc,j\sigma}\right)\right) + c.c. = 0 \tag{34}$$

where we have used the definitions

$$n_{j\sigma}(\mathbf{r}) := \varphi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}), \tag{35}$$

and the constants

$$\overline{v}^{KLI}_{xc,j\sigma} := \int \mathrm{d}^3 r \varphi^*_{j\sigma}(\mathbf{r}) v^{KLI}_{xc}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) \; . \tag{36}$$

The constants $\overline{u}_{xc,j\sigma}$ are defined in an analogous way as orbital averages of $u_{xc,j\sigma}(\mathbf{r})$ with respect to the orbital $\varphi_{j\sigma}$. Solving Eq. (34) for $v^{KLI}_{xc}(\mathbf{r})$ yields

$$v^{KLI}_{xc}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})}\sum_{\sigma=\uparrow,\downarrow}\sum_{j=1}^{N_\sigma} n_{j\sigma}(\mathbf{r})\left(u_{xc,j\sigma}(\mathbf{r}) + \overline{v}^{KLI}_{xc,j\sigma} - \overline{u}_{xc,j\sigma} + c.c.\right) \; . \tag{37}$$

This so-called KLI equation has transformed the OEP integral equation into an algebraic equation which is easier to solve in practical applications. Although this transformation is approximate, in many cases the deviations from full OEP results are small.

As we have seen, in the KLI approximation the Kohn-Sham orbital energy differences $\varepsilon_{j\sigma} - \varepsilon_{k\sigma}$ are approximated by one and the same constant, irrespective of the sign of different terms. In a similar spirit, a different approximation known as Common Energy Denominator Approximation (CEDA)[27] or Localized Hartree-Fock (LHF)[28] approximation has been proposed which only replaces the energy differences for occupied-unoccupied orbital pairs by a constant while it retains the energy differences for the occupied-occupied pairs. For the Green function this gives

$$G^{CEDA}_{s,j\sigma}(\mathbf{r},\mathbf{r}') = \sum_{\substack{k=1\\k\neq j}}^{N_\sigma} \frac{\varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} + \frac{1}{\Delta}\sum_{k>N_\sigma} \varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}') \; . \tag{38}$$

Adding and subtracting the contribution of the occupied orbitals with the common energy denominator and using the completeness of the Kohn-Sham orbitals yields

$$G^{CEDA}_{s,j\sigma}(\mathbf{r},\mathbf{r}') = \frac{\delta(\mathbf{r}-\mathbf{r}')}{\Delta} + \sum_{\substack{k=1\\k\neq j}}^{N_\sigma} \frac{\varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} - \frac{1}{\Delta}\sum_{k=1}^{N_\sigma} \varphi^*_{k\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}') \; , \tag{39}$$

which, when inserted into Eq. (25) leads to the following equation for the exchange-correlation potential in the CEDA approximation

$$\begin{aligned} v^{CEDA}_{xc}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Big(& n_{j\sigma}(\mathbf{r}) u_{xc,j\sigma}(\mathbf{r}) \\ & + \sum_{i=1}^{N_\sigma} \varphi^*_{i\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}) \left(\overline{v}^{CEDA}_{xc,ji\sigma} - \overline{u}_{xc,ji\sigma}\right) + c.c. \Big) \end{aligned} \tag{40}$$

with

$$\overline{v}^{CEDA}_{xc,ji\sigma} := \int \mathrm{d}^3 r \varphi^*_{j\sigma}(\mathbf{r}) v^{CEDA}_{xc}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \tag{41}$$

and similarly for $\overline{u}_{xc,ji\sigma}$. One immediately sees that the CEDA reduces to the KLI approximation if all off-diagonal terms $i \neq j$ in the second sum are neglected.

Both the KLI as well as the CEDA approximation (Eqs. (37) and (40), respectively) can easily be implemented within a self-consistent scheme with essentially the same effort. From a theoretical point of view, CEDA has the advantage of being invariant under unitary transformations of the occupied orbitals while KLI is not. From a practical point of view, CEDA and KLI results are often very similar.

3.3 Exact Transformation of the OEP Equation

In this section we discuss a way to transform the OEP equations exactly which both emphasizes the role of the orbital shifts (Eq. (27)) and allows to motivate the KLI approximation from a different perspective. We start by noting that the non-interacting Green function satisfies the following differential equations

$$\left(\hat{h}_s(\mathbf{r}) - \varepsilon_{j\sigma}\right) G_{s,j\sigma}(\mathbf{r}',\mathbf{r}) = -\left(\delta(\mathbf{r}-\mathbf{r}') - \varphi^*_{j\sigma}(\mathbf{r})\varphi_{j\sigma}(\mathbf{r}')\right) \tag{42}$$

where $\hat{h}_s(\mathbf{r})$ is the Kohn-Sham Hamiltonian. Acting with the operator $(\hat{h}_s(\mathbf{r}) - \varepsilon_{j\sigma})$ on Eq. (27) yields a differential equation which uniquely determines[18] the orbital shifts

$$\left(\hat{h}_s(\mathbf{r}) - \varepsilon_{j\sigma}\right) \psi^*_{j\sigma}(\mathbf{r}) = -\left(v_{xc}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - (\overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma})\right) \varphi^*_{j\sigma}(\mathbf{r}) \; . \tag{43}$$

Solving for $v_s(\mathbf{r})\psi^*_{j\sigma}(\mathbf{r})$ gives

$$\begin{aligned} v_s(\mathbf{r})\psi^*_{j\sigma}(\mathbf{r}) = &-\left(v_{xc}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - (\overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma})\right) \varphi^*_{j\sigma}(\mathbf{r}) \\ &+ \left(\frac{\nabla^2}{2} + \varepsilon_{j\sigma}\right) \psi^*_{j\sigma}(\mathbf{r}) \; . \end{aligned} \tag{44}$$

Multiplication of this equation with $\varphi_{j\sigma}$, subsequent summation over all occupied orbitals and using the OEP equation in the form (28) eventually leads to

$$\begin{aligned} v_{xc}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Bigg\{ & n_{j\sigma}(\mathbf{r}) \left(u_{xc,j\sigma}(\mathbf{r}) + \overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma}\right) \\ &+ \left(\frac{\nabla^2}{2}\psi^*_{j\sigma}(\mathbf{r}) + \varepsilon_{j\sigma}\psi^*_{j\sigma}(\mathbf{r})\right) \varphi_{j\sigma}(\mathbf{r}) + c.c. \Bigg\} \; . \end{aligned} \tag{45}$$

The second term in the curled brackets can be rewritten by using the Kohn-Sham equations and the OEP equation again which finally leads to an exact reformulation of the OEP equation as

$$\begin{aligned} v_{xc}(\mathbf{r}) = \frac{1}{2n(\mathbf{r})} \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Bigg\{ & n_{j\sigma}(\mathbf{r}) \left(u_{xc,j\sigma}(\mathbf{r}) + \overline{v}_{xc,j\sigma} - \overline{u}_{xc,j\sigma}\right) \\ &- \nabla \cdot \left(\psi^*_{j\sigma}(\mathbf{r}) \nabla \varphi_{j\sigma}(\mathbf{r})\right) + c.c. \Bigg\} \; . \end{aligned} \tag{46}$$

Clearly, if the term involving the orbital shifts $\psi^*_{j\sigma}(\mathbf{r})$ is neglected in this expression, one again obtains the KLI approximation.

The orbital shifts $\psi_{j\sigma}(\mathbf{r})$ also play a central role in an iterative scheme to the solution of the full OEP equation recently suggested by Kümmel and Perdew[19,20]. The idea of this scheme is to solve Eq. (43) for the orbital shifts directly in the following way: for a given approximate solution $v_{xc}(\mathbf{r})$ to the OEP equation, compute the right hand side of Eq. (43) and then solve this equation for the orbital shift $\psi_{j\sigma}(\mathbf{r})$ subject to the orthogonality constraint

$$\int \mathrm{d}^3 r \; \psi^*_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) = 0 \tag{47}$$

which follows from the definition in Eq. (27) by the orthonormality of the Kohn-Sham orbitals. With the resulting orbital shifts compute the quantity

$$S(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \psi^*_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) + c.c. \tag{48}$$

and then compute a new potential by

$$v^{\mathrm{new}}_{xc}(\mathbf{r}) = v^{\mathrm{old}}_{xc}(\mathbf{r}) + cS(\mathbf{r}) \tag{49}$$

with some positive constant c. With this new v_{xc}, recompute the right hand side of Eq. (43) and then solve again for a new orbital shift. This is iterated a few times for fixed $\varphi_{j\sigma}$, $\hat{h}_s$ and $\varepsilon_{j\sigma}$ before eventually these quantities are also recomputed during the regular Kohn-Sham self-consistency cycle. This scheme has been applied successfully[19,20] to compute the OEP potential (in exact exchange approximation) not only for highly symmetric systems such as atoms but also to small sodium clusters where a direct solution of the OEP integral equation (28) is a much more difficult task.

3.4 Derivative Discontinuity of the Exchange-Correlation Energy

Orbital dependent functionals have an important advantage over standard explicit density functionals like LDA or GGA: they may reproduce the derivative discontinuity of the exchange-correlation functional as a function of particle number which occurs at integer particle number N[29–31]. This is a very important property of the exact functional which was overlooked for a long time.

In order to discuss this property one has to generalize the definition (3) of the Hohenberg-Kohn functional to non-integer particle numbers, i.e., to densities with

$$\int \mathrm{d}^3 r \; n(\mathbf{r}) = N + \omega \tag{50}$$

where N is an integer and $0 \leq \omega \leq 1$. This generalization of the Hohenberg-Kohn functional can be given as

$$F_{frac}[n] = \min_{\hat{D}\to n} \mathrm{Tr}\left\{\hat{D}(\hat{T} + \hat{V}_{ee})\right\} \tag{51}$$

where the search runs over all statistical mixtures

$$\hat{D} = (1-\omega)|\Psi_N\rangle\langle\Psi_N| + \omega|\Psi_{N+1}\rangle\langle\Psi_{N+1}| \tag{52}$$

of an N-particle state $|\Psi_N\rangle$ and an $(N+1)$-particle state $|\Psi_{N+1}\rangle$ which yield the given density $n(\mathbf{r})$. The density and energy of the ensemble described by $\hat{D}$ are then given as

$$n(\mathbf{r}) = \mathrm{Tr}\left\{\hat{D}\,\hat{n}(\mathbf{r})\right\} = (1-\omega)n_N(\mathbf{r}) + \omega\, n_{N+1}(\mathbf{r}) \tag{53}$$

and

$$E_v[n] = F_{frac}[n] + \int \mathrm{d}^3 r \; v(\mathbf{r})n(\mathbf{r}) = (1-\omega)E_N + \omega E_{N+1} \tag{54}$$

where $n_N(\mathbf{r})$ and E_N are the density and energy corresponding to the state $|\Psi_N\rangle$ and similarly for n_{N+1} and E_{N+1}. Since the functional (Eq. (54)) is defined on the domain of densities with non-integer particle numbers, its minimum has to be found under the subsidiary condition of integer particle number which is incorporated by introducing the chemical potential μ as a the Lagrange multiplier. At the minimizing density, the variational equation then is

$$\mu(N) = \left.\frac{\delta E_v[n]}{\delta n(\mathbf{r})}\right|_{n_N} = \frac{\partial E_N}{\partial N} \tag{55}$$

Eqs. (54) and (55) show that the chemical potential $\mu(N)$ jumps discontinuously as N passes through an integer if E_N and E_{N+1} are separated by a finite energy gap. We can define this discontinuity as

$$\Delta(N) = \lim_{\omega \to 0} \left(\left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{n_{N+\omega}} - \left. \frac{\delta E_v[n]}{\delta n(\mathbf{r})} \right|_{n_{N-\omega}} \right) . \tag{56}$$

This expression can be written in terms of the ionization potential $I(N)$ and electronic affinity $A(N)$ of the N-particle system as

$$\Delta(N) = I(N) - A(N) = E(N+1) - 2E(N) + E(N-1) \tag{57}$$

where $E(N)$ is the ground state energy of the N-particle system. For infinite systems $\Delta(N)$ represents the so-called fundamental energy gap while for finite systems it is twice the chemical hardness. Insertion of Eq. (6) into Eq. (56) yields

$$\Delta(N) = \Delta_{KS}(N) + \Delta_{xc}(N) \tag{58}$$

where

$$\Delta_{KS} = \lim_{\omega \to 0} \left(\left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_{N+\omega}} - \left. \frac{\delta T_s[n]}{\delta n(\mathbf{r})} \right|_{n_{N-\omega}} \right) = \varepsilon_{N+1}(N) - \varepsilon_N(N) \tag{59}$$

is the Kohn-Sham gap. $\varepsilon_j(N)$ is the $j-$th Kohn-Sham energy eigenvalue of the N-particle system and

$$\Delta_{xc}(N) = \lim_{\omega \to 0} \left(\left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{n_{N+\omega}} - \left. \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right|_{n_{N-\omega}} \right) \tag{60}$$

is the derivative discontinuity of the exchange-correlation functional.

In Section 6.3 we will discuss some numerical results for the discontinuity and its contribution to the energy gap of semiconductors and insulators.

3.5 Orbital Functionals in Non-Collinear Spin Density Functional Theory

Until now we have discussed the OEP method in the framework of pure density functional theory, where only the particle density is used as fundamental variable. Spin-density functional theory (SDFT)[32] is an extension of the original DFT suited both for the description of systems with unpaired electrons and for systems in an external magnetic field. However, in SDFT only the coupling of the magnetic field to the spin degrees of freedom is taken into account. SDFT is mostly (but not always) applied under the assumption of collinear magnetism, i.e., both the external and Kohn-Sham magnetic field are assumed to have a constant direction in space and the magnetization vector is only allowed to be parallel or antiparallel to this given direction. In this situation, SDFT leads to two decoupled Kohn-Sham equations for spin-up and spin-down electrons. The OEP method is also well established for this situation. Here, however, we will present the OEP equations of SDFT without this restriction, i.e., for the non-collinear situation[33].

Instead of using Eq. (6), one usually starts by writing the ground-state energy $E_{v,\mathbf{B}}[n,\mathbf{m}]$ of a system of interacting electrons with ground state $|\Psi_0\rangle$ moving in the electrostatic potential $v(\mathbf{r})$ and the external magnetic field $\mathbf{B}(\mathbf{r})$ as

$$E_{v,\mathbf{B}}[n,\mathbf{m}] = T_s[n,\mathbf{m}] + \int \mathrm{d}^3 r\; v(\mathbf{r}) n(\mathbf{r}) - \int \mathrm{d}^3 r\; \mathbf{B}(\mathbf{r})\mathbf{m}(\mathbf{r}) + U[n] + E_{xc}[n,\mathbf{m}]\;. \quad (61)$$

Here, $E_{v,\mathbf{B}}$, T_s, and E_{xc} are expressed as functionals of the particle density

$$n(\mathbf{r}) = \langle \Psi_0 | \hat{\Psi}^\dagger(\mathbf{r}) \hat{\Psi}(\mathbf{r}) | \Psi_0 \rangle \quad (62)$$

and the magnetization density

$$\mathbf{m}(\mathbf{r}) = -\mu_B \langle \Psi_0 | \hat{\Psi}^\dagger(\mathbf{r}) \boldsymbol{\sigma} \hat{\Psi}(\mathbf{r}) | \Psi_0 \rangle \quad (63)$$

where $\hat{\Psi}(\mathbf{r})$ is the field operator for Pauli spinors, μ_B is the Bohr magneton and $\boldsymbol{\sigma}$ is the vector of Pauli matrices. Under the usual assumption of non-interacting v-representability, i.e., assuming that the densities $n(\mathbf{r})$ and $\mathbf{m}(\mathbf{r})$ can also be obtained as densities of a fictitious system of non-interacting electrons, one can then derive the Kohn-Sham equation

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r}) \right) \Phi_j(\mathbf{r}) = \varepsilon_j \Phi_j(\mathbf{r}) \quad (64)$$

where the $\Phi_i(\mathbf{r})$ are two-component, single-particle Pauli spinors. The effective potentials are given by

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int \mathrm{d}^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{xc}(\mathbf{r}) \quad (65)$$

with the exchange-correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n,\mathbf{m}]}{\delta n(\mathbf{r})} \quad (66)$$

and

$$\mathbf{B}_s(\mathbf{r}) = \mathbf{B}(\mathbf{r}) + \mathbf{B}_{xc}(\mathbf{r}) \quad (67)$$

with the exchange-correlation magnetic field

$$\mathbf{B}_{xc}(\mathbf{r}) = -\frac{\delta E_{xc}[n,\mathbf{m}]}{\delta \mathbf{m}(\mathbf{r})} \quad (68)$$

and the (universal) exchange-correlation energy functional $E_{xc}[n,\mathbf{m}]$ which has to be approximated in practice.

If E_{xc} is approximated as an *explicit* functional of n and $\mathbf{m}$, the functional derivatives (Eq. (66)) and (Eq. (68)) are easily evaluated. However, here we are more interested in the situation when E_{xc} is given as an explicit functional of the (spinor) orbitals (i.e., only as an *implicit* functional of the densities). Again, the exchange-correlation potentials need to be calculated with the OEP method described below. For simplicity, we assume that the approximate E_{xc} is given as a functional of the occupied spinors only, $E_{xc} = E_{xc}[\{\Phi_j\}]$. At this point, it should be noted that the spinor orbitals Φ_j (and therefore also $E_{xc}[\{\Phi_j\}]$) are, through Eq. (64), unique functionals of the potentials v_s and $\mathbf{B}_s$.

In order to obtain the OEP equations for the exchange-correlation potentials, we use the chain rule of functional derivatives to calculate

$$\begin{aligned}\frac{\delta E_{xc}}{\delta v_s(\mathbf{r})} &= \int \mathrm{d}^3 r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta v_s(\mathbf{r})} \right) \\ &= \sum_{k=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r}')} \frac{\delta \Phi_k(\mathbf{r}')}{\delta v_s(\mathbf{r})} + h.c. \right) \end{aligned} \tag{69}$$

and

$$\begin{aligned}\frac{\delta E_{xc}}{\delta \mathbf{B}_s(\mathbf{r})} &= \int \mathrm{d}^3 r' \left(v_{xc}(\mathbf{r}') \frac{\delta n(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} - \mathbf{B}_{xc}(\mathbf{r}') \frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} \right) \\ &= \sum_{k=1}^{N} \int \mathrm{d}^3 r' \left(\frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r}')} \frac{\delta \Phi_k(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + h.c. \right) \ . \end{aligned} \tag{70}$$

Using Eq. (64), the functional derivatives of the orbitals (and therefore also of the densities) with respect to the potentials can be computed from first-order perturbation theory. Following steps similar to the ones given in Section 3.1, one can write the OEP equations in the simple form

$$\sum_{k=1}^{N} \left(\Phi_k^\dagger(\mathbf{r}) \Psi_k(\mathbf{r}) + h.c. \right) = 0 \tag{71}$$

$$-\mu_B \sum_{k=1}^{N} \left(\Phi_k^\dagger(\mathbf{r}) \boldsymbol{\sigma} \Psi_k(\mathbf{r}) + h.c. \right) = 0 \tag{72}$$

where we have defined the orbital shifts[18–20]

$$\Psi_k(\mathbf{r}) = \sum_{\substack{j \\ j \neq k}} \frac{D_{kj} \Phi_j(\mathbf{r})}{\varepsilon_k - \varepsilon_j} \tag{73}$$

and

$$D_{kj} = \int \mathrm{d}^3 r' \, \Phi_j^\dagger(\mathbf{r}') \left(\left(v_{xc}(\mathbf{r}') + \mu_B \boldsymbol{\sigma} \mathbf{B}_{xc}(\mathbf{r}') \right) \Phi_k(\mathbf{r}') - \frac{\delta E_{xc}}{\delta \Phi_k^\dagger(\mathbf{r}')} \right) \ . \tag{74}$$

The OEP equations (71) and (72) can be interpreted in a simple manner: the optimized local potentials v_s and $\mathbf{B}_s$, i.e., the potentials giving the lowest total energy for a given energy functional, are the ones which yield a vanishing change in the density $n(\mathbf{r})$ and magnetization density $\mathbf{m}(\mathbf{r})$ in first-order perturbation theory when applying a perturbation $\hat{H}'$ to the Kohn-Sham equations where the perturbation is chosen such that the matrix elements with respect to the Kohn-Sham orbitals are given by $\langle \Phi_j | \hat{H}' | \Phi_k \rangle = -D_{kj}$.

Similar to the discussion in the previous section about the transformation of the OEP equation (28) to the form (46) in the DFT framework, one can also exactly transform the OEP equations (71) and (72) in non-collinear spin-DFT. Again, one starts with the differential equation for the orbital shifts

$$(\hat{h}_s(\mathbf{r}) - \varepsilon_k) \Psi_k(\mathbf{r}) = -\left(v_{xc}(\mathbf{r}) + \mu_B \boldsymbol{\sigma} \mathbf{B}_s(\mathbf{r}) \right) \Phi_k(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \Phi_k^\dagger(\mathbf{r})} + D_{kk} \Phi_k(\mathbf{r}) \ . \tag{75}$$

This equation, together with the OEP equations (71) and (72) eventually leads to the transformed OEP equations for non-collinear spin-DFT which may most conveniently be written in matrix notation as

$$\begin{pmatrix} n(\mathbf{r}) & -m_1(\mathbf{r}) & -m_2(\mathbf{r}) & -m_3(\mathbf{r}) \\ -m_1(\mathbf{r}) & \mu_B^2 n(\mathbf{r}) & 0 & 0 \\ -m_2(\mathbf{r}) & 0 & \mu_B^2 n(\mathbf{r}) & 0 \\ -m_3(\mathbf{r}) & 0 & 0 & \mu_B^2 n(\mathbf{r}) \end{pmatrix} \begin{pmatrix} v_{xc}(\mathbf{r}) \\ B_{xc,1}(\mathbf{r}) \\ B_{xc,2}(\mathbf{r}) \\ B_{xc,3}(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} g_1(\mathbf{r}) \\ g_2(\mathbf{r}) \\ g_3(\mathbf{r}) \\ g_4(\mathbf{r}) \end{pmatrix} \quad . \tag{76}$$

Here we have defined

$$g_1(\mathbf{r}) = \frac{1}{2} \sum_{k=1}^{N} \left(u_{xck}(\mathbf{r}) - \nabla \left((\nabla \Phi_k^\dagger(\mathbf{r})) \Psi_k(\mathbf{r}) \right) + n_k(\mathbf{r}) D_{kk} + h.c. \right) \tag{77}$$

with the orbital densities

$$n_k(\mathbf{r}) = \Phi_k^\dagger(\mathbf{r}) \Phi_k(\mathbf{r}) \tag{78}$$

and

$$u_{xck}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r})} \Phi_k(\mathbf{r}) \ . \tag{79}$$

The other terms on the right-hand side of Eq. (76) are given by

$$g_{\alpha+1}(\mathbf{r}) = \frac{\mu_B}{2} \sum_{k=1}^{N} \left(\tilde{u}_{xck,\alpha}(\mathbf{r}) - \nabla \left((\nabla \Phi_k^\dagger(\mathbf{r})) \sigma_\alpha \Psi_k(\mathbf{r}) \right) + m_{k,\alpha}(\mathbf{r}) D_{kk} + h.c. \right) \tag{80}$$

with $\alpha = 1, 2, 3$ and the Pauli matrices $\sigma_1 = \sigma_x$ etc. as well as the orbital magnetization

$$m_{k,\alpha}(\mathbf{r}) = -\mu_B \Phi_k^\dagger(\mathbf{r}) \sigma_\alpha \Phi_k(\mathbf{r}) \tag{81}$$

and

$$\tilde{u}_{xck,\alpha}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \Phi_k(\mathbf{r})} \sigma_\alpha \Phi_k(\mathbf{r}) \ . \tag{82}$$

Of course, under the common assumption that the Kohn-Sham exchange-correlation magnetic field has only a non-vanishing z-component, $\mathbf{B}_{xc}(\mathbf{r}) = (0, 0, B_{xc,3}(\mathbf{r}))^T$, out of the four equations of Eq. (76) only two are non-trivial and these can easily be transformed to the OEP equations of collinear spin-DFT[18].

4 Orbital Functionals for Exchange and Correlation

In this section we will discuss several ways towards the construction of orbital-dependent approximations to the exchange-correlation energy. We present some important concepts which offer some insight into the exchange-correlation energy and which serve as starting points for various approximate exchange-correlation functionals. We then give a brief overview over existing orbital functional approximations.

4.1 Adiabatic Connection

The adiabatic connection method[34–38] derives its name from the idea that one can connect the Hamiltonian of an interacting system to that of a non-interacting system via introduction of a coupling constant:

$$\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{V}_{ee} \ . \tag{83}$$

In the context of density functional theory, the external potential $\hat{V}_\lambda$ for the coupling constant λ is chosen such that the ground-state density of $\hat{H}_\lambda$ is independent of λ. For $\lambda = 1$, $\hat{V}_{\lambda=1}$ is just the external potential of the interacting system under consideration. Since for $\lambda = 0$ the ground state density of the corresponding non-interacting system is required to be equal to the density of the interacting system, $\hat{V}_{\lambda=0}$ is the corresponding Kohn-Sham potential.

In order to make the dependence of the results of this section on the strength of the electron-electron interaction explicit, we use

$$\hat{V}_{ee} = \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{84}$$

with e being the elementary charge.

The Hellmann-Feynman theorem for $\hat{H}_\lambda$ reads

$$\frac{dE_\lambda}{d\lambda} = \left\langle \Psi_n^{\min,\lambda} \middle| \frac{\partial \hat{H}_\lambda}{\partial \lambda} \middle| \Psi_n^{\min,\lambda} \right\rangle \tag{85}$$

where E_λ is the ground-state energy at coupling constant λ and $\Psi_n^{\min,\lambda}$ is the ground-state wave function of $\hat{H}_\lambda$, i.e., that wave function which yields the ground-state density $n(\mathbf{r})$ and minimizes the expectation value $\langle \hat{T} + \lambda \hat{V}_{ee} \rangle$. From Eq. (85), the following expression for the ground-state energy of the interacting system (at $\lambda = 1$) immediately follows:

$$E(\lambda = 1) = E_v[n] = T_s[n] + \int \mathrm{d}^3 r \ v(\mathbf{r}) n(\mathbf{r}) + \int_0^1 \mathrm{d}\lambda \ \langle \Psi_n^{\min,\lambda} | \hat{V}_{ee} | \Psi_n^{\min,\lambda} \rangle \ . \tag{86}$$

Comparison with Eq. (6) then yields an expression for the exchange-correlation energy,

$$E_{xc}[n] = \int_0^1 \mathrm{d}\lambda \ \langle \Psi_n^{\min,\lambda} | \hat{V}_{ee} | \Psi_n^{\min,\lambda} \rangle - U[n] =: \int_0^1 \mathrm{d}\lambda \ W_\lambda[n] \ , \tag{87}$$

where

$$W_\lambda[n] = \langle \Psi_n^{\min,\lambda} | \hat{V}_{ee} | \Psi_n^{\min,\lambda} \rangle - U[n] \ . \tag{88}$$

It is often convenient to partition $E_{xc}[n]$ into its exchange and correlation part,

$$E_{xc}[n] = E_x[n] + E_c[n] \ . \tag{89}$$

One may define the exchange energy as the value of the coupling-constant integrand (Eq. (88)) at $\lambda = 0$:

$$E_x[n] = W_{\lambda=0}[n] = \langle \Phi_n^{\min} | \hat{V}_{ee} | \Phi_n^{\min} \rangle - U[n] \tag{90}$$

where $\Phi_n^{\min}$ is the noninteracting ground-state wave function which yields n, i.e., the Kohn-Sham ground-state Slater determinant. Expressed in terms of single-particle orbitals, one obtains the usual Fock exchange energy expression of Eq. (17), i.e,

$$\begin{aligned} E_x[n] &= E_x^{EXX}[n] \\ &= -\frac{e^2}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{j,k=1}^{N_\sigma} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \ \frac{\varphi_{j\sigma}(\mathbf{r}) \varphi^*_{j\sigma}(\mathbf{r}') \varphi^*_{k\sigma}(\mathbf{r}) \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ . \end{aligned} \tag{91}$$

An alternative, but equivalent definition of the exchange energy makes use of uniform coordinate scaling[39]. Define a density

$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r}) \ , \tag{92}$$

which is scaled uniformly with a scaling parameter γ. Then, $E_x[n]$ is defined as the following limit

$$E_x[n] = \lim_{\gamma \to \infty} \frac{1}{\gamma} E_{xc}[n_\gamma] \tag{93}$$

which implies that E_x scales linearly under uniform coordinate scaling, i.e.

$$E_x[n_\gamma] = \gamma E_x[n] \ \ . \tag{94}$$

The relationship between the adiabatic connection and coordinate scaling extends much further than only for the definition of the exchange energy. Using coordinate scaling arguments, Görling and Levy[40] have suggested a perturbation expansion of the correlation energy in terms of the coupling constant λ. They were able to relate the λ-dependent external potential $v_\lambda(\mathbf{r})$ to functional derivatives at full coupling ($\lambda = 1$):

$$v_\lambda(\mathbf{r}) = v_{\lambda=0}(\mathbf{r}) - \lambda \left(v_H(\mathbf{r}) + v_x(\mathbf{r}) + \lambda \frac{\delta E_c[n_{1/\lambda}]}{\delta n(\mathbf{r})} \right) \tag{95}$$

where the Hartree potential is given by Eq. (12) and the exchange potentials is

$$v_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})} \ . \tag{96}$$

Görling and Levy used Eq. (95) to calculate the ground state energy of $\hat{H}_\lambda$ with perturbation theory in the expansion parameter λ. To first order, the result is (at full coupling, $\lambda = 1$):

$$E^{(0)}[n] + E^{(1)}[n] = T_s[n] + \int \mathrm{d}^3 r \ v(\mathbf{r}) n(\mathbf{r}) + U[n] + E_x[n] \tag{97}$$

which is formally identical to the Hartree-Fock energy expression evaluated with Kohn-Sham orbitals. The second-order term is given by

$$\begin{aligned} E^{(2)}[n] &= E_c^{GL2}[n] \\ &= \frac{1}{2} \sum_{\sigma,\sigma'} \sum_{\varepsilon_{i\sigma}, \varepsilon_{j\sigma'} \le \varepsilon_F < \varepsilon_{k\sigma}, \varepsilon_{l\sigma'}} \frac{(ik\sigma||jl\sigma')[(jl\sigma'||ik\sigma) - \delta_{\sigma,\sigma'}(jl\sigma||ki\sigma)]}{\varepsilon_{i\sigma} + \varepsilon_{j\sigma'} - \varepsilon_{k\sigma} - \varepsilon_{l\sigma'}} \\ &\quad + \sum_\sigma \sum_{\varepsilon_{i\sigma} \le \varepsilon_F < \varepsilon_{l\sigma}} \frac{1}{\varepsilon_{i\sigma} - \varepsilon_{l\sigma}} \left| \langle i\sigma | v_x | l\sigma \rangle + \sum_{\varepsilon_{j\sigma} \le \varepsilon_F} (ij\sigma||jl\sigma) \right|^2 \end{aligned} \tag{98}$$

where we have defined the two-electron integral

$$(ik\sigma||jl\sigma') = \int \mathrm{d}^3r \int \mathrm{d}^3r' \; \varphi^*_{i\sigma}(\mathbf{r})\varphi_{k\sigma}(\mathbf{r}) \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \varphi^*_{j\sigma'}(\mathbf{r}')\varphi_{l\sigma'}(\mathbf{r}') \tag{99}$$

and

$$\langle i\sigma|v_x|j\sigma'\rangle = \int \mathrm{d}^3r \; \varphi^*_{i\sigma}(\mathbf{r}) v_x(\mathbf{r}) \varphi_{j\sigma'}(\mathbf{r}) \; . \tag{100}$$

The similarity to traditional quantum-chemical methods is again apparent. The first term in Eq. (98) is the familiar energy expression of second-order Møller-Plesset perturbation theory (see, e.g., Ref. 41) while the second term originates from the first-order correction of the Kohn-Sham Slater determinant towards the Hartree-Fock wave function. As the exchange energy could be defined through coordinate scaling (Eq. (93)), the second-order correlation energy may also be obtained as the $\gamma \to \infty$ limit of the correlation energy under uniform coordinate scaling,

$$E_c^{GL2}[n] = \lim_{\gamma\to\infty} E_c[n_\gamma] > -\infty \; . \tag{101}$$

The inequality sign only applies to densities which integrate to a finite number of electrons[42].

Both E_x of Eq. (91) and E_c^{GL2} of Eq. (98) are given explicitly in terms of the Kohn-Sham orbitals (and orbital energies) and the corresponding exchange and correlation potentials have to be calculated using the OEP method. While the exchange energy $E_x[n]$ is only a functional of the occupied orbitals, E_c^{GL2} also is a functional of all the unoccupied orbitals and the orbital energies.

4.2 Fluctuation-Dissipation Theorem

A different representation of E_{xc}, which we want to introduce now, relates the exchange-correlation energy to the (dynamic) density-density response function of the interacting system of interest. Obviously, the description of response functions requires a formal extension of density functional theory to the time-dependent domain[43]. The central ideas of time-dependent density functional theory (TDDFT) are completely analogous to the static case (for a review of TDDFT, see Ref. 44). One first proves a one-to-one mapping between time-dependent external potentials and time-dependent densities, then one constructs an auxiliary non-interacting system with the same time-dependent density as the interacting system. The equations to describe this auxiliary system have the structure of a Schrödinger equation for non-interacting electrons moving in a time-dependent, local single-particle potential $v_s(\mathbf{r},t)$.

As the name implies, the linear density response function χ describes the change of the density $\delta n(\mathbf{r},t)$ in response to some external time-dependent perturbation $\delta v(\mathbf{r},t)$:

$$\delta n(\mathbf{r},t) = \int_{t_0}^{t} \mathrm{d}t' \; \int \mathrm{d}^3r \; \chi(\mathbf{r},\mathbf{r}',t-t')\delta v(\mathbf{r}',t') \; . \tag{102}$$

We assume that the system is in its ground state before the perturbation is switched on at time t_0. Using the fluctuation-dissipation theorem at zero temperature, one can express

the exchange-correlation energy in terms of the Fourier transform of the linear density response function:

$$E_{xc}[n] = \frac{1}{2}\int_0^1 \mathrm{d}\lambda \int\mathrm{d}^3r \int\mathrm{d}^3r' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \left(-\frac{1}{\pi}\int_0^\infty \mathrm{d}\omega\ \mathrm{Im}\,\chi^\lambda(\mathbf{r},\mathbf{r}',\omega) - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right) . \tag{103}$$

Again, we have used the idea of the adiabatic connection, i.e., we consider the interacting response function χ^λ for a scaled electron-electron interaction $\lambda e^2/|\mathbf{r}-\mathbf{r}'|$ while the density is kept fixed for all values of λ.

The time-dependent Kohn-Sham scheme allows to calculate the interacting density response function as solution of the following integral equation which relates χ^λ to the response function χ_s of the non-interacting Kohn-Sham system[45,46]:

$$\chi^\lambda(\mathbf{r},\mathbf{r}',\omega) = \chi_s(\mathbf{r},\mathbf{r}',\omega) + \int\mathrm{d}^3x\int\mathrm{d}^3y\ \chi_s(\mathbf{r},\mathbf{x},\omega)\left(\frac{\lambda e^2}{|\mathbf{x}-\mathbf{y}|} + f_{xc}^\lambda(\mathbf{x},\mathbf{y},\omega)\right)\chi^\lambda(\mathbf{y},\mathbf{r}',\omega) . \tag{104}$$

Here, the so-called exchange-correlation kernel is defined as functional derivative of the time-dependent exchange-correlation potential, evaluated at the ground-state density of the static (unperturbed) system:

$$f_{xc}^\lambda(\mathbf{r},\mathbf{r}',\omega) = \int \mathrm{d}(t-t')\ \exp(i\omega(t-t'))\frac{\delta v_{xc}^\lambda[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}\bigg|_{n(\mathbf{r},t)=n(\mathbf{r})} . \tag{105}$$

The Kohn-Sham linear density response function χ_s may be expressed in terms of the Kohn-Sham orbitals and orbital energies through

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) = \sum_\sigma\sum_{i,j}(f_{i\sigma}-f_{j\sigma})\frac{\varphi_{i\sigma}^*(\mathbf{r})\varphi_{j\sigma}(\mathbf{r})\varphi_{j\sigma}^*(\mathbf{r}')\varphi_{i\sigma}(\mathbf{r}')}{\omega-(\varepsilon_{j\sigma}-\varepsilon_{i\sigma})+i\delta} \tag{106}$$

where $f_{i\sigma}$ is the occupation number (0 or 1) of the orbital $\varphi_{i\sigma}(\mathbf{r})$ in the Kohn-Sham ground-state Slater determinant. Insertion of Eqs. (106) and (104) into Eq. (103) represents the exact exchange-correlation energy as an explicitly orbital-dependent functional.

It should be noted that, similar to Görling-Levy perturbation theory of the previous section, also the representation (Eq. (103)) allows for E_{xc} to be expanded in a power series in e^2, i.e.,

$$E_{xc} = \sum_{j=1}^\infty e^{2j}E_{xc}^{(j)} = E_x + E_c^{(2)} + \ldots \tag{107}$$

where the Fock exchange energy constitutes the first-order and E_c^{GL2} of Eq. (98) the second-order term. The series (Eq. (107)) has to be understood as a series expansion of the *functional* E_{xc} which can be evaluated with any set of single-particle orbitals. In particular, it usually is evaluated on the Kohn-Sham orbitals which themselves (through the Kohn-Sham potential v_s) also depend on e^2.

Since the exchange-correlation potential is computed from E_{xc} as the functional derivative (Eq. (13)), Eq. (107) implies that also v_{xc} can be written as a power series in

e^2,

$$v_{xc}(\mathbf{r}) = \sum_{j=1}^{\infty} e^{2j} v_{xc}^{(j)}(\mathbf{r}) = v_x(\mathbf{r}) + v_c^{(2)}(\mathbf{r}) + \ldots \tag{108}$$

where the first order term is again the exact exchange contribution.

In a sense, the representation (Eq. (103)) of E_{xc} is much more powerful than the Görling-Levy expansion. While the latter provides an order-by-order expansion of E_{xc}, the former provides a prescription for resummation of an infinite power series if for the response function χ^λ one inserts a solution of the integral equation (104). The simplest of these resummed functionals is the so-called random phase approximation (RPA) which results if the exchange-correlation kernel is set to zero, $f_{xc}^{RPA} \equiv 0$.

4.3 Exact Exchange Energy

As we have seen in the previous section, the exact exchange energy functional (Eq. (91)) is nothing but the Fock term evaluated with Kohn-Sham orbitals and may be viewed as the leading term in a power series expansion of E_{xc} in powers of e^2. Moreover, if one does not include any correlation, the corresponding total energy functional (97) is exactly of the Hartree-Fock form. Therefore a comparison between exact-exchange only DFT and Hartree-Fock theory is instructive.

In Hartree-Fock theory, the energy functional (Eq. (97)) is minimized with respect to the orbitals without restriction leading to the non-local Hartree-Fock potential. Consequently, the Hartree-Fock ground state Slater determinant gives the lowest energy when inserted into the Hartree-Fock energy functional. In contrast, in exchange-only OEP (EXX) one minimizes the same functional under the constraint that the orbitals are eigenfunctions to one and the same *local* potential. Since this minimization is not unconstrained, the resulting total energy from the OEP orbitals must be higher than the Hartree-Fock energy. However, OEP gives the optimal local potential and therefore any approximate local potential such as exchange-only KLI or CEDA yields orbitals which, when inserted into the Hartree-Fock energy expression, lead to total energies higher than the OEP ones. In practice, it turns out that total energies in Hartree-Fock are typically very close to exchange-only OEP, KLI and CEDA results.

Both Hartree-Fock and EXX theories are free of self-interaction for the occupied orbitals. This means that the orbital $\varphi_{i\sigma}$ does not "feel" the electrostatic potential formally created by itself as part of the Hartree potential because this term is exactly cancelled by a corresponding term in the exchange potential. It should be noted that standard functionals like LDA or GGA do not have this property. Moreover, while the Hartree-Fock potential is *not* self-interaction free for unoccupied states, the EXX potential is. As a consequence, Hartree-Fock only leads to few unoccupied bound states. On the other hand, the EXX potential decays asymptotically as $-1/r$ for finite systems for *all* orbitals and therefore supports a whole Rydberg series of unoccupied bound states.

The latter statement needs some clarification. It is generally said that the EXX potential for finite systems behaves as[22, 25, 47]

$$\lim_{r\to\infty} v_x^{EXX}(\mathbf{r}) \to -\frac{1}{r} \,. \tag{109}$$

Although this statement is true for $\mathbf{r}$ far away from the system in most directions, it has been found[48,20] that if one approaches the asymptotic region on nodal surfaces of the highest occupied orbital the Kohn-Sham exchange potential may actually approach a non-vanishing constant value.

For metals, the Hartree-Fock single-particle density of states at the Fermi energy vanishes. This unphysical feature does not appear for the EXX density of states.

4.4 Correlation Energy Functionals from GL2 to RPA and Beyond

Although both the adiabatic connection method of Section 4.1 as well as the fluctuation-dissipation theorem of Section 4.2 provide a way to construct orbital functionals for the correlation energy, much less work has been done using these functionals than with the EXX functional. The reason is mainly a practical one: while EXX depends on the occupied orbitals only, these functionals for correlation depend on *all* Kohn-Sham orbitals, occupied and unoccupied, as well as on the Kohn-Sham eigenenergies. Although the OEP equations for the corresponding correlation potentials can easily be written down, their solution is much more difficult in practice. However, some features of these orbital functionals for correlation are known and further investigation of their properties appears both interesting and promising.

One of the interesting properties of orbital-dependent correlation energy functionals is their ability to give the proper C_6/R^6 long-range van-der-Waals contribution to the total energy for two closed-shell atoms separated by distance R. Zaremba and Kohn[49] have derived an expression for the C_6 van-der-Waals coefficient in terms of the dynamic polarizability of the separated subsystems. The latter can easily be expressed in terms of the linear density response function of Eq. (104). C_6 coefficients have been evaluated[50] for some atoms using an approximate linear response function where χ on the right hand side of Eq. (104) is replaced by the Kohn-Sham linear response function χ_s and the PGG approximation[46] for the exchange-correlation kernel f_{xc} was used. The results were found to be accurate to within 10-20 % for light atoms but considerably worse for heavier ones.

Along similar lines, Engel et. al.[51] have mapped out the binding energy curve of rare gas dimers as a function of atomic separation using the Görling-Levy second order functional of Eq. (98). They found a qualitatively correct description, however, a full quantitative description apparently requires higher-order correlations to be taken into account.

The results of Refs. 50 and 51 were obtained from non-selfconsistent calculations. In more recent work[52] a problem with the self-consistent calculation of the correlation potential from the second-order functional (Eq. (98)) has been pointed out. It was found that for finite systems the corresponding correlation potential diverges exponentially for large distances r. This is in contrast to an exact result[53] which says that the exact correlation potential decays asymptotically as $\sim 1/r^4$. The work of Facco Bonetti et. al.[52] has sparked a discussion[54,55] where theoretical arguments have been put forward which indicate that the correct asymptotic behavior can only be obtained when subtle cancellation effects (related to the exact closure relation and discretization of the continuum) are taken into account[56]. Self-consistent calculations for atoms using E_c^{GL2} have also been performed in a basis set representation in Ref. 57.

Recently, there has been some effort in going beyond the second-order approximation and use Eq. (103) with a density response function which solves the Dyson-like equation

(104) for some approximation to the exchange-correlation kernel f_{xc}. Non-selfconsistent calculations have been performed in RPA and beyond, both for simple model systems such as jellium slabs[58] but also for molecules[59,60]. For molecules, also van-der-Waals binding energy curves for rare-gas dimers have been calculated[60].

It is known that in order to construct a correlation energy functional which is compatible with exact exchange, the correlation part has to cancel the long-range part of the exact exchange hole. Local functionals like LDA or GGA have a local correlation hole and therefore combination of these functionals with exact exchange is less accurate than if also an LDA or GGA approximation for exchange is used. The correlation energy functionals discussed in this section have a chance to be compatible with exact exchange due to their nonlocal nature. In fact, a functional has been constructed which uses E_c^{GL2} as input and interpolates the coupling-constant integrand W_λ of Eq. (88). This so-called interaction strength interpolation (ISI) functional has been demonstrated to give accurate results for molecular atomization energies when combined with exact exchange[61].

4.5 Self-Interaction Correction to LDA

Unlike the exact exchange functional discussed in Section 4.3, explicit density functionals like LDA or GGA typically are not free of self-interaction, i.e., the exchange-correlation energy does not cancel exactly the self-interaction contained in the Hartree energy (Eq. (5)). One of the consequences is the incorrect exponential asymptotic decay of the corresponding exchange-correlation potentials for finite systems.

Some time ago, Perdew and Zunger[7] suggested to make any approximate E_{xc}^{approx} self-interaction free by removing the self-interaction explicitly for each orbital. Their self-interaction corrected (SIC) exchange-correlation energy is constructed by (in the formulation of collinear spin-DFT)

$$E_{xc}^{SIC}[n_\uparrow, n_\downarrow] = E_{xc}^{approx}[n_\uparrow, n_\downarrow] - \sum_{\sigma=\uparrow,\downarrow} \sum_{j=1}^{N_\sigma} \Big(U[n_{j\sigma}] + E_{xc}^{approx}[n_{j\sigma}, 0] \Big) \qquad (110)$$

where the $n_{j\sigma}(\mathbf{r})$ are the orbital densities defined by Eq. (35). In the original work[7], the corresponding total energy functional was minimized with respect to the orbitals, leading to orbital-dependent effective single-particle potentials. However, Eq. (110) certainly is an orbital-dependent functional and may therefore be treated with the OEP formalism[62].

The self-interaction correction should be particularly important for localized orbitals such as d- or f-states in transition metals or rare earths. The SIC functional has successfully been applied to such materials in the solid state[63,64]. However, here it is important that the functional is *not* evaluated with the Kohn-Sham eigenstates, since in a solid these states are Bloch orbitals and often extend throughout the whole system. For such extended states, the self-interaction correction vanishes. Therefore, in order to apply SIC, one has to construct localized orbitals which are then used to evaluate the SIC correction.

4.6 Other Orbital Functionals: Hybrids and Meta-GGA's

Finally we want to discuss two other classes of functionals which fall into the domain of orbital functionals.

One of them are the so-called hybrid functionals which are constructed by approximating the exchange energy by a *fraction* of exact exchange plus some GGA part for the remainder, i.e.,

$$E_x^{hyb}[n] = aE_x^{EXX}[n] + (1-a)E_x^{GGA}[n] \tag{111}$$

where a is a constant parameter. Usually, this approximate exchange functional is combined with some GGA for correlation. Hybrids have been introduced in quantum chemistry[65–68] and have been found to yield accurate results for many energetic properties. Probably the most widely known hybrid functional is the three-parameter functional with the acronym B3LYP which is defined by

$$E_{xc}^{B3LYP}[n] = E_{xc}^{LDA}[n] + a_0(E_x^{EXX}[n] - E_x^{LDA}[n]) + a_x E_x^{B88}[n] + a_c E_c^{LYP}[n] \tag{112}$$

Here E_x^{B88} is the GGA exchange energy of Becke[14]. E_c^{LYP} is the GGA correlation functional suggested by Lee, Yang, and Parr[15] which is derived from the explicitly orbital-dependent functional of Colle and Salvetti[69].

Hybrid functionals are implemented in a wide range of quantum chemistry program packages. Interpretation of the results of these packages, however, requires some care. The reason is that the self-consistency cycle in many cases does not use the OEP method or any approximation to it to evaluate the corresponding effective single-particle potentials. Instead, the results are obtained by minimizing the energy expression with respect to the single-particle orbitals. Due to the appearance of the Fock term $E_x^{EXX}[n]$ in the energy expression, this leads to *non-local* effective single-particle potentials and thus the results are outside the realm of density functional theory.

The second class of functionals we would like to mention here are the so-called meta-GGA's[70–72] which are of the general form

$$E_{xc}^{MGGA}[n] = \int \mathrm{d}^3r \; g(n, \nabla n, \tau) \tag{113}$$

where

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 \tag{114}$$

is the kinetic energy density of the Kohn-Sham orbitals. Through their dependence on τ, meta-GGA's also become orbital functionals and their exchange-correlation potentials have to be calculated with the OEP method. As in the case of the hybrids, this is not always done. However, meta-GGA's have been implemented self-consistently in the LHF approximation to OEP to calculate magnetic response properties[73].

5 The LDA+U Method

In this section we will discuss a method which has been used to describe strongly correlated systems in a modified DFT framework. This method uses insights gained from studies of model Hamiltonians for strong correlations like the Hubbard model[74] and tries to incorporate them into the density functional framework. The resulting so-called LDA+U method[75] has been found, e.g., to correctly predict the antiferromagnetic insulating ground state of La_2CuO_4[76]. Although usually the LDA+U procedure is not discussed in the context of the

OEP method, structural similarities to DFT with an orbital-dependent energy functional may also be found here.

The rationale behind the LDA+U method is the observation that the LDA does not properly describe strongly correlated systems such as transition metal oxides or rare-earth compounds where localized d- and f-electrons play an important role. One tries to correct the LDA treatment of those orbitals and to identify those regions of space (usually "atomic spheres") where the atomic character of the localized orbitals has survived. Within these spheres one expands the electronic states in a localized basis $|inlm\sigma\rangle$ of atomic eigenstates where i is a site index, n is the principal quantum number, l the angular momentum, m the magnetic quantum number and σ the spin index. For simplicity, we restrict ourselves to situations where only one particular nl shell is contributing. The matrix elements of the density matrix for this shell are then given by

$$f^{\sigma}_{mm'} = -\frac{1}{\pi}\int^{\varepsilon_F} \mathrm{d}E\ \mathrm{Im}\left(G^{s,\sigma}_{inlm;inlm'}(E)\right) \tag{115}$$

where $G^{s,\sigma}_{inlm;inlm'}(E) = \langle inlm\sigma|(E-\hat{H}^s)^{-1}|inlm'\sigma\rangle$ is the matrix element of the single-particle Green's function corresponding to the non-interacting Hamiltonian $\hat{H}_s$. One then writes the total energy functional in the LDA+U method in terms of the matrix elements (Eq. (115)) as[77]

$$E^{LDA+U}[n,\{f^{\sigma}\}] = E^{LDA}[n] + E^{U}[\{f^{\sigma}\}] - E^{dc}[\{f^{\sigma}\}]\ . \tag{116}$$

Here, $E^{LDA}[n]$ is the usual LDA total energy functional and

$$\begin{aligned} E^{U}[\{f^{\sigma}\}] = \frac{1}{2}\sum_{\{m\},\sigma}^{loc} \Big(& \langle mm''|\hat{V}^{scr}_{ee}|m'm'''\rangle f^{\sigma}_{mm'} f^{-\sigma}_{m''m'''} \\ & + \Big(\langle mm''|\hat{V}^{scr}_{ee}|m'm'''\rangle - \langle mm''|\hat{V}^{scr}_{ee}|m'''m'\rangle\Big) f^{\sigma}_{mm'} f^{\sigma}_{m''m'''}\Big) \end{aligned} \tag{117}$$

where $\hat{V}^{scr}_{ee}$ is the screened Coulomb interaction between the nl electrons and the sum runs only over these localized states. Finally, $E_{dc}[\{f^{\sigma}\}]$ corrects for double counting and is given by

$$E^{dc}[\{f^{\sigma}\}] = \frac{1}{2}UN(N-1) - \frac{1}{2}J\left(N_{\uparrow}(N_{\uparrow}-1) + N_{\downarrow}(N_{\downarrow}-1)\right) \tag{118}$$

where N_{σ} is the number of σ electrons in the nl shell and $N = N_{\uparrow} + N_{\downarrow}$. U is the Hubbard parameter which is an average measure for the on-site (screened) Coulomb interaction while, similarly, J is an average (screened) exchange parameter.

Eqs. (116), (117), and (118) define the total energy in terms of the localized basis functions $|inlm'\sigma\rangle$ which is somewhat unusual. In order to get some insight into the nature of this definition we consider the very simple case of an isolated atom. We further take $\hat{H}_s$ as the Kohn-Sham Hamiltonian corresponding to the LDA+U energy functional. It should be noted that this is a deviation from the LDA+U procedure as it is typically applied in the literature. There the Hamiltonian is orbital dependent and results from a minimization of Eq. (116) with respect to the orbitals.

One now can choose the eigenfunctions for such an atomic, orbital-independent $\hat{H}_s$ as basis $|inlm\sigma\rangle$. Then the density matrix (115) becomes diagonal, $f^{\sigma}_{mm'} = f^{\sigma}_{mm}\delta_{m,m'}$ and

the energy E^U reads

$$E^U[\{f^\sigma\}] = \frac{1}{2}\sum_{\{m\},\sigma}^{loc}\Big(\langle mm'|\hat{V}_{ee}^{scr}|mm'\rangle f_{mm}^{\sigma} f_{m'm'}^{-\sigma} + \Big(\langle mm'|\hat{V}_{ee}^{scr}|mm'\rangle - \langle mm'|\hat{V}_{ee}^{scr}|m'm\rangle\Big) f_{mm}^{\sigma} f_{m'm'}^{\sigma}\Big) . \quad (119)$$

This can be rewritten in terms of the density

$$n^{loc}(\mathbf{r}) = \sum_{\{m\}}^{loc} f_{mm}^{\sigma} |\varphi_{nlm\sigma}(\mathbf{r})|^2 \quad (120)$$

and single-particle density matrix

$$\gamma_{\sigma}^{loc}(\mathbf{r},\mathbf{r}') = \sum_{\{m\},\sigma}^{loc} f_{mm}^{\sigma} \varphi_{nlm\sigma}^{*}(\mathbf{r})\varphi_{nlm\sigma}(\mathbf{r}') \quad (121)$$

of the localized states as an Hartree-Fock-like energy with respect to the screened interaction, i.e,

$$E^U[\{\varphi_{nlm\sigma}\}] = \frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r'\; n^{loc}(\mathbf{r}) V_{ee}^{scr}(\mathbf{r},\mathbf{r}') n^{loc}(\mathbf{r}') - \frac{1}{2}\sum_{\sigma}\int \mathrm{d}^3r \int \mathrm{d}^3r'\; |\gamma_{\sigma}^{loc}(\mathbf{r},\mathbf{r}')|^2 V_{ee}^{scr}(\mathbf{r},\mathbf{r}') . \quad (122)$$

This shows that the LDA+U functional tries to correct LDA by treating localized orbitals on a Hartree-Fock-like footing with respect to the screened interaction. The connection between the screened interaction in the LDA+U method and the screened Coulomb interaction of Hedin's GW approach[78] has been discussed in Ref. 79. In practice one expresses the matrix elements of the screened interaction V_{ee}^{scr} in terms of known Slater integrals and the parameters U and J which are determined from LDA supercell calculations[75,77,79].

For simplicity, we discussed only the case of an isolated atom but it is clear that one can view the LDA+U method in the framework of orbital functionals for any system if the functional E^U of Eq.(122) is interpreted as a functional of the *localized* Kohn-Sham orbitals only. Of course, this requires a selection of a set of localized orbitals by physical insight into the system under consideration.

In a sense the LDA+U method is similar to the philosophy both of the self-interaction corrected (SIC) functional of Section 4.5 and the hybrids of Section 4.6. It is similar to SIC because Eq. (122) is free of self-interaction of the localized orbitals by construction. These are the orbitals for which the self-interaction error of LDA is largest. On the other hand it is similar to the hybrids because it uses a fraction of "screened" exchange, although not in a global sense but by correcting only a particular set of orbitals, i.e., the localized ones.

6 Numerical Results

In this section we report some results obtained with the OEP method for various systems ranging from atoms and molecules to solids. The selection of results presented is, of

course, both subjective and incomplete. We concentrate on results obtained with the exact exchange functional and, if data are available, correlation energy functionals either from perturbation theory or from the fluctuation-dissipation formula.

6.1 Atoms

We start by presenting some results of exchange-only calculations for atoms using the exact exchange functional in spin-unrestricted OEP and KLI, as well as pure exchange-only spin density funtionals such as LDA, Becke's GGA for exchange (B88)[14] and the Perdew-Wang GGA (PW91)[16]. Spin-unrestricted Hartree-Fock[80] (SUHF) energies are also given as a reference. In Table 1 we present total ground state energies in these different approximations for atoms with nuclear charge $Z \leqslant 10$. Results for heavier atoms can be found, e.g., in Ref. 18. The calculations have been done solving the radial part of the Schroedinger equation by the Numerov method. For open shell configurations the Kohn-Sham potential has been calculated with fractional occupation of all orbitals within this shell. This kind of angular averaging leads to spherically symmetric Kohn-Sham potentials and the angular part can be treated analytically.

We first compare the SUHF and exchange-only OEP results. In this case, the two schemes differ only in the constraints used when minimizing the same total energy functional. In the OEP method, the minimization is subject to the constraint that the single-particle wave functions are eigenfunctions of one *local* effective potential. In the Hartree-Fock method, one computes those orbitals which minimize the Hartree-Fock total energy without any constraint (except orthonormality) and a non local effective potential is obtained. As a consequence of the additional constraint, the OEP total energies have to be higher (or equal at best) than the corresponding SUHF ones. This is confirmed by the data in Table (1). It can also be seen that the OEP total energies are very close to the SUHF results.

Comparing the KLI with the OEP results one sees that the KLI approximation gives higher total energies for almost all cases except for one- and two-electron systems for

Atom	SUHF	OEP	KLI	B88	PW91	LDA
H	0.5000	0.5000	0.5000	0.4979	0.4953	0.4571
He	2.8617	2.8617	2.8617	2.8634	2.8552	2.7236
Li	7.4328	7.4325	7.4324	7.4288	7.4172	7.1934
Be	14.5730	14.5724	14.5723	14.5664	14.5543	14.2233
B	24.5293	24.5283	24.5281	24.5173	24.5035	24.0636
C	37.6900	37.6889	37.6887	37.6819	37.6658	37.1119
N	54.4046	54.4034	54.4030	54.4009	54.3824	53.7093
O	74.8136	74.8121	74.8117	74.8148	74.7964	73.9919
F	99.4108	99.4092	99.4087	99.4326	99.4130	98.4740
Ne	128.5471	128.5454	128.5448	128.5901	128.5689	127.4907

Table 1. Absolute ground state energies (in atomic units) for different exchange-only approximations. Values are taken from[18] and references therein.

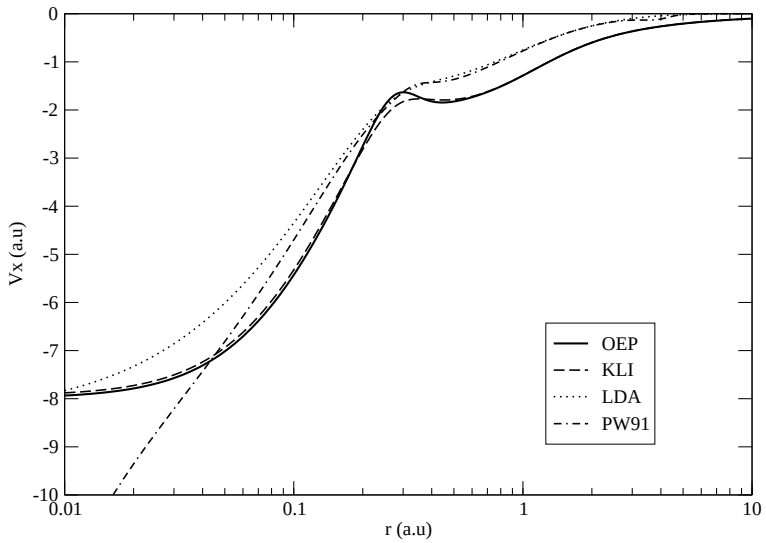

Figure 1. Exchange potentials for Ne from various self-consistent exchange-only calculations.

which the KLI approximation is exact and coincides with both OEP and HF. The difference between KLI and OEP total energies is in general very small. Moreover it tends to decrease almost monotonically with increasing atomic numbers. At least from the point of view of the total energies, the KLI scheme provides a very good approximation to the full OEP results. This statement is often true also for other quantities such as single-particle eigenvalues and potentials. However, as we will see later, there are properties for which the KLI approximation is not so accurate.

Comparing OEP results with those of standard density functionals, one sees that LDA and OEP total energies show large differences. Something can be gained by considering GGA functionals such as B88 and PW91. It should be noted that for some atoms the GGA functionals give total energies lower than OEP.

In Figure 1 we show the self-consistent exchange potentials for the Ne atom in various approximations. Unlike the exact exchange functional both LDA and GGA's suffer from the self-interaction error. The self-interaction energy contained in the Hartree energy is not exactly cancelled by LDA or GGA exchange which leads to the incorrect asymptotic behavior of the corresponding potentials: both LDA and GGA potentials decay exponentially fast far away from the nucleus. On the other hand, both OEP and KLI potentials are free of self-interaction and therefore their asymptotics is dominated by the $-\frac{1}{r}$ term. The KLI potential follows the OEP potential rather closely in most regions of space. The difference is largest in the atomic inter-shell region where the OEP potentials shows a pronounced hump while in the KLI potential the hump is less prominent.

The self-interaction problem has another consequence as well. Since both LDA and GGA potentials decay exponentially fast, a neutral atom does not exhibit a Rydberg series of excited states in these approximations. Also, negative ions are not stable. On the other hand, OEP and KLI both show a Rydberg series and are also able to support negative

Atom/Ion	KLI		BLYP	PW91	exact
	EXX	EXX+CS			
He	0.9180	0.9446	0.5849	0.5833	0.9037
Be^{2+}	5.6671	5.6992	4.8760	4.8701	5.6556
Be	0.3089	0.3294	0.2009	0.2072	0.3426
C^{2+}	1.6933	1.7226	1.4804	1.4856	1.7594
Ne	0.8494	0.8841	0.4914	0.4942	0.7945
Na^{+}	1.7959	1.8340	1.3377	1.3416	1.7410

Table 2. Ionization potentials (in a.u.) from highest occupied Kohn-Sham orbital energies for different exchange-correlation functionals. EXX+CS are results for the exact exchange functional combined with the orbital functional for correlation of Ref. 69 in KLI approximation. Values are taken from Ref. 18.

ions. Moreover, if one calculates the ionization potential as the negative eigenvalue of the highest occupied Kohn-Sham orbital[53] one finds a much better agreement with experiment in OEP than in GGA. This is illustrated for some atoms and ions in Table 2.

While in OEP the self-interaction is absent for both occupied and unoccupied orbitals, in Hartree-Fock only the occupied orbitals are self-interaction free. Therefore the unoccupied orbitals in Hartree-Fock are usually too high in energy leading to HOMO-LUMO gaps which are too large.

In Section 3.2, in addition to the KLI approximation we also discussed a slightly modified approximate scheme for the solution of the OEP equation, the CEDA approximation. How do CEDA results compare to OEP or KLI ones? As a matter of fact, total energies, single-particle energies and potentials of atoms are very close to each other in the three different schemes[81]. Table 3 shows atomic ground state energy differences between CEDA and SUHF as well as KLI and SUHF results. One can see that the KLI and CEDA ground state energies are nearly identical. It should be mentioned here, however, that CEDA and KLI results not for all properties agree so well among each other. An example where CEDA and KLI results are not so close will be discussed in Section 6.2.

Finally, in Table 4 we report some results for atomic correlation energies from evaluation of Eq. (103) with different approximations for the linear response function. The results were obtained for two different exchange-correlation kernels, the RPA kernel $f_{xc}^{RPA} \equiv 0$ and the kernel f_{xc}^{PGG} of Petersilka et. al.[46]. The second order correlation energies were obtained by inserting the response function obtained from Eq. (104) with χ^{λ} on the right

Atom	$E^{KLI} - E^{SUHF}$	$E^{CEDA} - E^{SUHF}$
Be	0.00060	0.00060
Ne	0.0022	0.0022
Ar	0.0048	0.0052

Table 3. Atomic energy differences between KLI, CEDA and HF total energies (in hartrees). Values taken from Ref. 81.

Atom	second order		infinite order		exact
	$f_{xc}=0$	f_{xc}^{PGG}	$f_{xc}=0$	f_{xc}^{PGG}	
He	0.0961	0.0481	0.0830	0.0444	0.0420
Be	0.2419	0.1254	0.1753	0.1011	0.0950
Ne	0.7157	0.4013	0.5799	0.3293	0.3929

Table 4. Atomic correlation energies (-E_c in hartrees) in second order and to infinite order for different exchange-correlation kernels. Exact results are from Ref. 82.

hand side replaced by χ_s. The results to infinite order used the response function solving the integral equation (104) for the given approximate f_{xc}. The results are evaluated with exchange-only KLI orbitals represented with the Slater-type basis set used in Ref. 83.

6.2 Molecules

DFT with orbital functionals has been applied to molecular systems as well. The first results were obtained with the KLI approximation[84–86]. Later, both CEDA[81] and full OEP results were reported[87,88,20]. For total energies, binding energies and vibrational frequencies the exchange-only KLI, CEDA, and OEP results are rather close to each other and also close to Hartree-Fock values. In Table 5 we show few deviations of total ground state energies from Hartree-Fock results both in KLI and CEDA approximations which are almost identical.

For molecular binding energies, exchange-only KLI, CEDA, and OEP results are of rather poor quality. The errors, which are close to Hartree-Fock errors, are on average more than twice as large as in LDA and almost an order of magnitude worse than GGA results[88]. This is not unexpected since the exchange hole has a long-range component in the dissociation limit which has to be compensated by a corresponding long-range component of the correlation hole. Correlation functionals with this property are notoriously difficult to construct[61]. Combination of the exact exchange energy with LDA or GGA correlation leads to some improvement, leading to errors for the atomization energies of the same order of magnitude as LDA results (but typically with the opposite sign). This confirms that the success of explicit functionals relies on an error cancellation between the approximate exchange and correlation parts of the total energy.

Not for all properties KLI, CEDA and OEP results are so similar as for total energies and related quantities. Quite large differences emerge[81] for linear and non-linear response

Molecule	$E^{KLI}-E^{HF}$	$E^{CEDA}-E^{HF}$
N_2	0.0078	0.0077
CO	0.0076	0.0076
H_2O	0.00392	0.00364

Table 5. Molecular energies differences between KLI, CEDA and HF total energies (in hartrees). Values from Ref. 81.

α	H_4	H_6	H_8	H_{12}	H_{18}
HF	32.0	56.4	82.3	137.6	222.3
OEP	32.2	56.6	84.2	138.1	
CEDA		59.3		149.4	244.2
KLI	33.1	60.2	90.6	156.3	260.7

Table 6. Linear polarizabilities α (in a.u.) for different hydrogen chains in various exchange-only treatments. Values from Ref. 89 and Ref. 81.

properties of molecular chains where the high mobility of the valence electrons along the backbone leads to a large directional electronic response.

The response properties of these molecular chains can be characterized by the linear polarizabilities α and the hyperpolarizabilities γ, defined as the first and third derivatives, $\partial\mu_z/\partial E_z$ and $\partial^3\mu_z/\partial^3 E_z$, of the dipole moment μ_z with respect to the electric field E_z along the direction of the chain, respectively.

In LDA and GGA α and γ are usually overestimated by orders of magnitude in comparison to Hartree-Fock results which are in reasonable agreement with results obtained from correlated quantum chemical methods[81,89]. KLI and CEDA values give some improvement over standard functionals. This is due to the orbital structure of the CEDA and KLI exchange potentials which produces an exchange field counteracting the external field. Moreover, there are pronounced differences between KLI and CEDA results (see Tables 6 and 7). The latter gives considerable improvement as compared to KLI, but in order to reach Hartree-Fock quality a full solution of the OEP equations is required[89].

Some molecular calculations using RPA-type correlation energy functionals have been reported recently[59,60,90]. RPA atomization energies are much improved over EXX ones[59,60] with an error close to but slightly worse than standard GGA functionals. Similar results were obtained with kernels derived from standard GGA's[60].

The binding energy curve of the H_2 molecule has been studied in detail in Ref. 90 using the RPA functional (in a non-selfconsistent way). There the total density obtained from unrestricted exchange-only calculations is used to obtain an accurate *spin-restricted* Kohn-Sham potential. The orbitals resulting from this potential are then used as input for the RPA calculation. The resulting ground state energies are accurate not only around equilibrium bond length but also at larger interatomic separation beyond the Coulson-Fisher point.

$\gamma/10^3$	H_4	H_6	H_8	H_{12}	H_{18}
HF		29.8		147	301.3
OEP	9.3	30	68	144	
CEDA		34.7		209.2	468.4
KLI	10.7	36	90	300	778.1

Table 7. Hyperpolarizabilities γ (in a.u.) for different hydrogen chains in various exchange-only treatments. Values from Ref. 89 and Ref. 81.

However at intermediate separations an unphysical bump appears, which may be due to the absence of double excitations in adiabatic linear response theory. Similar results are obtained for RPA-like functionals if the exact exchange kernel is included. In another work[91] a different orbital-dependent exchange-correlation functional has been employed in the OEP framework within the CEDA approximation reproducing very well the entire H_2 potential curve.

6.3 Solids

A number of successful applications of the exact exchange functional have been reported for solids. The first application is due to Kotani[92], who treated the exact exchange potential within the linear muffin-tin-orbital method in the atomic-sphere approximation. Later, Görling[93] proposed a procedure to solve the OEP equation for a solid exactly in a plane wave basis. This technique was then applied[94,95] to several semiconductors. In the same work, the exchange discontinuity Δ_x has been computed as well.

Lattice constants predicted by exact exchange plus LDA correlation generally agree as well with experiment as the full LDA ones[95]. On the other hand, bulk moduli are overestimated and a treatment of correlations beyond LDA is needed[95].

Probably the most interesting result of these calculations are the ones for the band gaps of semiconductors. Standard functionals such as LDA or GGA typically give Kohn-Sham band gaps which are too small, often by a factor of two. This is a manifestation of two main shortcomings of these functionals: on the one hand there is the self-interaction error and on the other hand they fail to reproduce a finite derivative discontinuity.

The exact exchange functional eliminates the self-interaction problem and the corresponding Kohn-Sham gaps often provide excellent estimates for the experimental gaps as can be seen in Table 8. On the other hand, EXX also leads to a derivative discontinuity Δ_x which is actually quite large. If this is included in the calculation of the gap, the agreement is ruined and the gaps are too large. This finding can also be understood from a different perspective: in Eq. (57) we have expressed the fundamental gap in terms of total energies of the $N-1$, N, and $N+1$-particle system. Experience tells us that EXX and Hartree-Fock total energies are very close. Therefore the fundamental gap in EXX is expected to be close to the Hartree-Fock gap which is usually far too large.

Not always the EXX Kohn-Sham gaps are in such a good agreement with experimental gaps as in semiconductors. In Table 9 we show some results for noble-gas solids[96]. We see that the Kohn-Sham gaps differ from the fundamental band gaps by several eV and

Solid	xcLDA	EXX+cLDA	Δ_x	Exp.
Si	0.52	1.43	5.84	1.17
C	4.16	5.06	8.70	5.47
GaN (Γ)	1.90	3.46	7.63	3.30
InN (Γ)	-0.18	1.40	6.14	1.95

Table 8. Calculated Kohn-Sham and experimental energy gaps in in semiconductors (in eV). EXX is exact exchange, cLDA denotes correlation in LDA. Values taken from[94] and references therein.

Solid	Δ_{KS}	Δ_{exp}	Δ_{opt}
Ne	14.15	21.4	17.4
Ar	9.61	14.2	12.2
Kr	7.87	11.6	10.2
Xe	6.69	9.8	8.4

Table 9. Calculated Kohn-Sham gaps, Δ_{KS}, and experimental fundamental energy gaps, Δ_{exp}, in noble-gas solids (in eV). Δ_{opt} is the experimental optical gap. Values taken from Ref. 96.

reproduce about 80% of the experimental optical gaps.

Very recently, self-consistent RPA calculations have been performed to study the band gap problem[97]. To simplify the calculation, a plasmon pole approximation for the RPA (or GW) self-energy was used. The resulting Kohn-Sham gaps turned out to be rather close to LDA results, i.e., they were considerably smaller than Kohn-Sham gaps from EXX calculations. However, if the exchange-correlation discontinuity was taken into account, the resulting gaps were close to GW and experimental gaps.

As a final application of the OEP formalism to extended systems we mention a very recent calculation within the non-collinear spin-DFT framework[33] for a magnetically frustrated monolayer of chromium which shows how intra-atomic non-collinearity may be underestimated by local functionals.

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References

1. P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:B864, 1964.
2. M. Levy. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem. *Proc. Natl. Acad. Sci. USA*, 76:6062, 1979.
3. M. Levy. Electron densities in search of Hamiltonians. *Phys. Rev. A*, 26:1200, 1982.
4. W. Kohn and L.J. Sham. Self-consistent equations including exchange and correlation. *Phys. Rev.*, 140:A1133, 1965.
5. D.M. Ceperley and B.J. Alder. Ground State of the Electron Gas by a Stochastic Method. *Phys. Rev. Lett.*, 45:566, 1980.
6. S.H. Vosko, L. Wilk, and M. Nusair. Accurate spin-dependent electron liquid correlation energies for local spin-density calculations - a critical analysis. *Can. J. Phys.*, 58:1200, 1980.
7. J.P. Perdew and A. Zunger. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*, 23:5048, 1981.

8. J.P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron gas correlation energy. *Phys. Rev. B*, 45:13244, 1992.
9. S.-K. Ma and K.A. Brueckner. Correlation Energy of an Electron Gas with a Slowly Varying High Density. *Phys. Rev.*, 165:18, 1968.
10. M. Rasolt and D.J.W. Geldart. Exchange and correlation energy in a nonuniform fermion fluid. *Phys. Rev. B*, 34:1325, 1986.
11. J.P. Perdew. Accurate Density Functional for the Energy: Real-Space Cutoff of the Gradient Expansion for the Exchange Hole. *Phys. Rev. Lett.*, 55:1665, 1985.
12. J.P. Perdew and Y. Wang. Accurate and simple exchange functional for the electronic exchange energy: Generalized gradient approximation. *Phys. Rev. B*, 33:8800, 1986. ibid. **40**, 3399 (1989) (E).
13. A.D. Becke. Density functional calculations of molecular bond energies. *J. Chem. Phys.*, 84:4524, 1986.
14. A.D. Becke. Density functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A*, 38:3098, 1988.
15. C. Lee, W. Yang, and R.G. Parr. Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev. B*, 37:785, 1988.
16. J.P. Perdew. Unified theory of exchange and correlation beyond the local density approximation. In P. Ziesche and H. Eschrig, editors, *Electronic Structure of Solids '91*, page 11, Berlin, 1991. Akademie Verlag.
17. J.P. Perdew, K. Burke, and M. Ernzerhof. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 77:3865, 1996. ibid. **78**, 1396 (1997)(E).
18. T. Grabo, T. Kreibich, S. Kurth, and E.K.U. Gross. Orbital functionals in density functional theory: the optimized effective potential method. In V. Anisimov, editor, *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond Local Density Approximations*, page 203, Amsterdam, 2000. Gordon and Breach.
19. S. Kümmel and J.P. Perdew. Simple iterative construction of the optimized effective potential for orbital functionals, including exact exchange. *Phys. Rev. Lett.*, 90:043004, 2003.
20. S. Kümmel and J.P. Perdew. Optimized effective potential made simple: Orbital functionals, orbital shifts, and the exact Kohn-Sham exchange potential. *Phys. Rev. B*, 68:035103, 2003.
21. R.T. Sharp and G.K. Horton. A Variational Approach to the Unipotential Many-Electron Problem. *Phys. Rev.*, 90:317, 1953.
22. J.D. Talman and W.F. Shadwick. Optimized effective atomic central potential. *Phys. Rev. A*, 14:36, 1976.
23. V. Sahni, J. Gruenebaum, and J.P. Perdew. Study of the density-gradient expansion for the exchange energy. *Phys. Rev. B*, 26:4371, 1982.
24. J.P. Perdew and M.R. Norman. Electron removal energies in Kohn-Sham density-functional theory. *Phys. Rev. B*, 26:5445, 1982.
25. J.B. Krieger, Y. Li, and G.J. Iafrate. Construction and application of an accurate local spin-polarized Kohn-Sham potential with integer discontinuity: Exchange-only theory. *Phys. Rev. A*, 45:101, 1992.
26. J.B. Krieger, Y. Li, and G.J. Iafrate. Systematic approximations to the optimized effective potential: Application to orbital-density-functional theory. *Phys. Rev. A*, 46:5453, 1992.

27. O.V. Gritsenko and E.J. Baerends. Orbital structure of the Kohn-Sham exchange potential and exchange kernel and the field-counteracting potential for molecules in an electric field. *Phys. Rev. A*, 64:42506, 2001.
28. F. Della Sala and A. Görling. Efficient localized Hartree-Fock methods as effective exact-exchange Kohn-Sham methods for molecules. *J. Chem. Phys.*, 115:5718, 2001.
29. J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz. Density functional theory for fractional particle number: Derivative discontinuity of the energy. *Phys. Rev. Lett.*, 49:1691, 1982.
30. L.J. Sham and M. Schlüter. Density-functional theory of the energy gap. *Phys. Rev. Lett.*, 51:1888, 1983.
31. L.J. Sham and M. Schlüter. Density-functional theory of the band gap. *Phys. Rev. B*, 32:3883, 1985.
32. U. von Barth and L. Hedin. A local exchange-correlation potential for the spin polarized case. *J. Phys. C*, 5:1629, 1972.
33. S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, N. Helbig, S. Kurth, E.K.U. Gross, S. Shallcross, and L. Nordström. Optimized effective potential method for non-collinear magnetism. cond-mat/0510800 (2005).
34. J. Harris and R.O. Jones. The surface energy of a bounded electron gas. *J. Phys. F*, 4:1170, 1974.
35. D.C. Langreth and J.P. Perdew. The exchange-correlation energy of a metallic surface. *Solid State Commun.*, 17:1425, 1975.
36. D.C. Langreth and J.P. Perdew. Exchange-correlation energy of a metallic surface: Wavevector analysis. *Phys. Rev. B*, 15:2884, 1977.
37. O. Gunnarsson and B.I. Lundqvist. Exchange and correlation in atoms, molecules, and solids by the spin-density-functional formalism. *Phys. Rev. B*, 13:4274, 1976.
38. A. Görling, M. Levy, and J.P. Perdew. Expectation values in density-functional theory, and kinetic contribution to the exchange-correlation energy. *Phys. Rev. B*, 47:1167, 1993.
39. M. Levy and J.P. Perdew. Hellmann-Feynman, virial, and scaling requisites for the exact universal density functionals. shape of the correlation potential and diamagnetic susceptibility for atoms. *Phys. Rev. A*, 32:2010, 1985.
40. A. Görling and M. Levy. Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion. *Phys. Rev. B*, 47:13105, 1993.
41. A. Szabo and N.S. Ostlund. *Modern Quantum Chemistry*. MacMillan, New York, 1982.
42. M. Levy. Density-functional exchange correlation through coordinate scaling in adiabatic connection and correlation hole. *Phys. Rev. A*, 43:4637, 1991.
43. E. Runge and E.K.U. Gross. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.*, 52:997, 1984.
44. E.K.U. Gross, J.F. Dobson, and M. Petersilka. Density functional theory of time-dependent phenomena. In R.F. Nalewajski, editor, *Density Functional Theory II*, volume 181 of *Topics in Current Chemistry*, page 81. Springer, Berlin, 1996.
45. E.K.U. Gross and W. Kohn. Time-dependent density-functional theory. *Adv. Quantum Chem.*, 21:255, 1990.
46. M. Petersilka, U.J. Gossmann, and E.K.U. Gross. Excitation energies from time-

dependent density-functional theory. *Phys. Rev. Lett.*, 76:1212, 1996.
47. T. Kreibich, S. Kurth, T. Grabo, and E.K.U. Gross. Asymptotic Properties of the Optimized Effective Potential. *Adv. Quantum Chem.*, 33:31, 1999.
48. F. Della Sala and A. Görling. The asymptotic region of the Kohn-Sham exchange potential in molecules. *J. Chem. Phys.*, 116:5374, 2002.
49. E. Zaremba and W. Kohn. Van der Waals interaction between an atom and a solid surface. *Phys. Rev. B*, 13:2270, 1976.
50. M. Lein, J.F. Dobson, and E.K.U. Gross. Towards the description of van der Waals interactions within density functional theory. *J. Comput. Chem.*, 20:12, 1999.
51. E. Engel, A. Höck, and R.M. Dreizler. Van der Waals bonds in density functional theory. *Phys. Rev. A*, 61:032502, 2000.
52. A. Facco Bonetti, E. Engel, R.N. Schmid, and R.M. Dreizler. Investigation of the correlation potential from Kohn-Sham perturbation theory. *Phys. Rev. Lett.*, 86:2241, 2001.
53. C.O. Almbladh and U. von Barth. Exact results for the charge and spin densities, exchange-correlation potentials, and density-functional eigenvalues. *Phys. Rev. B*, 31:3231, 1985.
54. Y.M. Niquet, M. Fuchs, and X. Gonze. Comment on "Investigation of the correlation potential from Kohn-Sham perturbation theory". *Phys. Rev. Lett.*, 90:219301, 2003.
55. A. Facco Bonetti, E. Engel, R.N. Schmid, and R.M. Dreizler. Reply to Y.M. Niquet, M. Fuchs and X. Gonze. *Phys. Rev. Lett.*, 90:219302, 2003.
56. Y.M. Niquet, M. Fuchs, and X. Gonze. Asymptotic behavior of the exchange--correlation potentials from the linear-response Sham-Schlüter equation. *J. Chem. Phys.*, 118:9504, 2003.
57. I. Grabowski, S. Hirata, S. Ivanov, and R.J. Bartlett. Ab initio density functional theory: OEP-MBPT(2). A new orbital-dependent correlation functional. *J. Phys. Chem.*, 116:4415, 2002.
58. J.F. Dobson, J. Wang, and T. Gould. Correlation energies of inhomogeneous many-electron systems. *Phys. Rev. B*, 66:081108(R), 2002.
59. F. Furche. Molecular tests of the random phase approximation to the exchange-correlation energy functional. *Phys. Rev. B*, 64:195120, 2001.
60. F. Furche and T. Van Voorhis. Fluctuation-dissipation theorem density-functional theory. *J. Chem. Phys.*, 122:164106, 2005.
61. M. Seidl, J.P. Perdew, and S. Kurth. Simulation of all-order density functional perturbation theory, using the second-order and the strong-correlation limit. *Phys. Rev. Lett.*, 84:5070, 2000.
62. J. Chen, J.B. Krieger, Y. Li, and G.J. Iafrate. Kohn-Sham calculations with self-interaction-corrected local-spin-density exchange-correlation energy functional for atomic systems. *Phys. Rev. A*, 54:3939, 1996.
63. A. Svane and O. Gunnarsson. Transition-metal oxides in the self-interaction-corrected density-functional formalism. *Phys. Rev. Lett.*, 65:1148, 1990.
64. Z. Szotek, W.M. Temmerman, and H. Winter. Self-interaction corrected, local spin density description of the γ - α transition in Ce. *Phys. Rev. Lett.*, 72:1244, 1994.
65. A.D. Becke. A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.*, 98:1372, 1993.
66. A.D. Becke. Density-functional thermochemistry: III. The role of exact exchange.

J. Chem. Phys., 98:5648, 1993.
67. A.D. Becke. Density-functional thermochemistry: IV. A new dynamical correlation functional and implications for exact-exchange mixing. *J. Chem. Phys.*, 104:1040, 1996.
68. C. Adamo and V. Barone. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.*, 110:6158, 1999.
69. R. Colle and O. Salvetti. Approximate calculation of the correlation energy for closed shells. *Theoret. Chim. Acta*, 37:329, 1975.
70. J.P. Perdew, S. Kurth, A. Zupan, and P. Blaha. Accurate density functional with correct formal properties: A step beyond the generalized gradient approximation. *Phys. Rev. Lett.*, 82:2544, 1999. ibid. **82**, 5179 (1999)(E).
71. S. Kurth, J.P. Perdew, and P. Blaha. Molecular and solid state tests of density functional approximations: LSD, GGA's, and Meta-GGA's. *Int. J. Quantum Chem.*, 75:889, 1999.
72. J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria. Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett.*, 91:146401, 2003.
73. A.V. Arbuznikov and M. Kaupp. The self-consistent implementation of exchange--correlation functionals depending on the local kinetic energy density. *Chem. Phys. Lett.*, 381:495, 2003.
74. J. Hubbard. Electron correlations in narrow energy bands. *Proc. R. Soc. London*, A 276:238, 1963.
75. V.I. Anisimov, J. Zaanen, and O.K. Andersen. Band theory and Mott insulators: Hubbard U and Stoner J. *Phys. Rev. B*, 44:943, 1991.
76. M.T. Czyżyk and G.A. Sawatzky. Local-density functional and on-site correlations: The electronic structure of La_2CuO_4 and $LaCuO_3$. *Phys. Rev. B*, 49:14211, 1994.
77. A.I. Liechtenstein, V.I. Anisimov, and J. Zaanen. Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. *Phys. Rev. B*, 52:R5467, 1995.
78. L. Hedin. New method for calculating the one-particle Green's function with application to the electron-gas problem. *Phys. Rev.*, 139:A796, 1965.
79. V.I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein. First-principles calculations of the electronic structure and spectra of strongly correlated systems: the LDA+U method. *J. Phys. Condens. Matter*, 9:767, 1997.
80. Y. Li, J.B. Krieger, and G.J. Iafrate. Self-consistent calculations of atomic properties using self-interaction-free exchange-only Kohn-Sham potentials. *Phys. Rev. A*, 47:165, 1993.
81. M. Grüning, O.V. Gritsenko, and E.J. Baerends. Exchange potential from the common energy denominator approximation for the Kohn-Sham Green's function: Application to (hyper)polarizabilities of molecular chains. *J. Chem. Phys.*, 116:6435, 2002.
82. J.B. Krieger, J. Chen, G.J. Iafrate, and A. Savin. Construction of an accurate self-interaction-corrected correlation energy functional based on an electron gas with a gap. In A. Gonis and N. Kioussis, editors, *Electron Correlations and Materials Properties*, page 463, New York, 1999. Plenum.
83. N.E. Dahlen and U. von Barth. Variational second-order Møller-Plesset theory based on the Luttinger-Ward functional. *J. Chem. Phys.*, 120:6826, 2004.

84. T. Grabo and E.K.U. Gross. The optimized effective potential method of density functional theory: Applications to atomic and molecular systems. *Int. J. Quantum Chem.*, 64:95, 1997.
85. Y.-H. Kim, M. Städele, and R.M. Martin. Density-functional study of small molecules within the Krieger-Li-Iafrate approximation. *Phys. Rev. A*, 60:3633, 1999.
86. E. Engel, A. Höck, and R.M. Dreizler. Accuracy of the Krieger-Li-Iafrate approximation for molecules. *Phys. Rev. A*, 62:042502, 2000.
87. S. Ivanov, S. Hirata, and R.J. Bartlett. Exact exchange treatment for molecules in finite-basis-set Kohn-Sham theory. *Phys. Rev. Lett.*, 83:5455, 1999.
88. A. Görling. New KS method for molecules based on an exchange charge density generating the exact local KS exchange potential. *Phys. Rev. Lett.*, 83:5459, 1999.
89. S. Kümmel, L. Kronik, and J.P. Perdew. Electrical response of molecular chains from density functional theory. *Phys. Rev. Lett.*, 93:213002, 2004.
90. M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke. Describing static correlation in bond dissociation by Kohn-Sham density functional theory. *J. Chem. Phys.*, 122:094116, 2005.
91. M. Grüning, O.V. Gritsenko, and E.J. Baerends. Exact exchange-correlation treatment of dissociating H_2 in density functional theory. *J. Chem. Phys.*, 118:7183, 2003.
92. T. Kotani. Exact exchange-potential band-structure calculations by the LMTO-ASA method: MgO and CaO. *Phys. Rev. B*, 50:14816, 1994.
93. A. Görling. Exact treatment of exchange in Kohn-Sham band-structure schemes. *Phys. Rev. B*, 53:7024, 1996.
94. M. Städele, J.A. Majewski, P. Vogl, and A. Görling. Exact Kohn-Sham exchange potential in semiconductors. *Phys. Rev. Lett.*, 79:2089, 1997.
95. M. Städele, M. Moukara, J.A. Majewski, P. Vogl, and A. Görling. Exact exchange Kohn-Sham formalism applied to semiconductors. *Phys. Rev. B*, 59:10031, 1999.
96. R. Magyar, A. Fleszar, and E.K.U. Gross. Exact-exchange density-functional calculations for noble-gas solids. *Phys. Rev. B*, 69:045111, 2004.
97. M. Grüning, A. Marini, and A. Rubio. Unpublished.